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<b>(21) International Application Number:</b> PCT/US99/30790 <b>(22) International Filing Date:</b> 22 December 1999 (22.12.99) <b>(30) Priority Data:</b> 09/223,664 30 December 1998 (30.12.98) US <b>(71) Applicant:</b> THE B.F. GOODRICH COMPANY [US/US]; 4020 Kinross Lakes Parkway, Richfield, OH 44286 (US). <b>(72) Inventors:</b> GALLEGUILLOS, Ramiro; 5645 Williamsburg Circle, Hudson, OH 44236 (US). SMITH, David, J.; 613 Winesap Road, Amherst, OH 44001 (US). CONSTANTINO, Steven, P.; 14623 LaGrange Road, LaGrange, OH 44050 (US). <b>(74) Agents:</b> HUDAK, Daniel, J.; Hudak & Shunk Co., L.P.A., Suite 808, 7 West Bowery Street, Akron, OH 44308-1133 (US) et al.		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** BRANCHED/BLOCK COPOLYMERS FOR TREATMENT OF KERATINOUS SUBSTRATES

**(57) Abstract**

A block copolymer for hair styling compositions includes hydrophilic and hydrophobic blocks which allow for optimization of desirable characteristics of the hair styling composition, such as style retention at high humidity, tack, hardness, resistance to flaking, and washability from the hair. The copolymer includes a polyacrylate backbone of hydrophobic blocks, with hydrophilic acrylate side chains. The copolymer is suitable for the formulation of a number personal care, household, hair care, skin care and other formulation. The copolymer is suited to incorporation into low VOC hydra-alcoholic hair styling compositions to meet reduced VOC, regulations.

Typical hair styling polymers are random copolymers which are prepared by polymerizing two or more hydrophilic, anionic, cationic, or hydrophobic monomers, such as acrylic or vinyl monomers. The backbone of the resulting polymer is typically composed of a statistically random distribution of all the monomers. The ratio of these monomers is selected in such a way as to obtain a resin with a certain hydrophilic and hydrophobic balance.

The hydrophobic monomers generally provide better hairstyle retention at high humidity levels. Polymers, in which hydrophobic monomers predominate heavily, however, have poor solubility in water-ethanol mixtures, are not readily washable from the hair, and tend to flake and feel plastic-like on the hair. They are therefore unsuited to use in hair styling formulations.

On the other hand, polymers with high levels of hydrophilic groups have good solubility in water/ethanol mixtures and are washable from the hair. However, they are generally too sensitive to moisture, becoming tacky, and therefore do not hold a hairstyle under conditions of high humidity. U.S. Patent No. 3,954,960 to Valan, for example, discloses a random copolymer of purely hydrophilic monomers. This is a film-forming resin of a quaternized copolymer of vinyl pyrrolidone and a copolymerizable vinyl monomer such as a di-lower alkyl alkyaminoalkyl (or hydroxy alkyl) acrylate or methacrylate. Quaternized polymers of polyvinyl pyrrolidone, however, tend to be highly moisture sensitive and have overall poor performance in hairstyle retention and tack.

Accordingly, it is desirable to build a resin with a balance of hydrophilic and hydrophobic groups to achieve a combination of performance properties, such as style retention at high humidity, tack, hardness, flaking, washability from the hair, and other subjective performance attributes.

A typical example of a random copolymer having a hydrophilic/hydrophobic balance is disclosed in U.S. Patent No. 3,914,403 to Valan. Valan discloses a film-forming resin formed from polyvinyl pyrrolidone, vinyl acetate, and a cationic monomer. The polyvinyl pyrrolidone and the cationic groups form the hydrophilic portion of the resin, while vinyl acetate provides the hydrophobic portion. By varying the ratio of polyvinyl pyrrolidone to vinyl acetate, water soluble or water insoluble polymers are obtained. The highly water soluble polymers tend to have poor

hair style retention at high humidity, whereas the highly insoluble ones are likely to be un-washable and too plastic-like.

U.S. Patent No. 3,925,542 to Viout, et al. and U.S. Patent No. 5,196,495 to Chuang, et al. disclose additional examples of random copolymers with various hydrophilic/hydrophobic balances. Uses for the copolymers include aerosols, lacquers, non-aerosol hair sprays, hair setting creams, and setting lotions.

U.S. Patent No. 4,007,005 to Patel discloses a hair setting resin based on a random copolymer of a reactive polyamide epichlorohydrin and polyvinyl pyrrolidone. The copolymer provides long style retention at high humidity. However, the reactive polymers are toxic and lack washability from the hair when used as aerosols, non-aerosol hair sprays and setting lotions.

Due to environmental regulations controlling the emission of volatile organic compounds (VOC's) into the atmosphere, VOC emissions have been restricted to 80% by weight of the hair styling formulation in some states, with further restrictions to 55% anticipated. To meet the regulations, reduced VOC hair styling formulations are being developed. Water is substituted for part or all of the organic solvents conventionally used in such formulations. U.S. Patent No. 5,565,193 to Midha, et al. discloses a random copolymer hairstyling resin primarily formed from monomers such as n-butyl acrylate (the hydrophobic component), and acrylic acid, the (hydrophilic component), grafted with siloxane to balance the properties and to render the resin suitable for formulation in an 80% VOC composition. However, such polymers tend to become too soft and produce negative beading on the hair in low VOC formulations.

U.S. Patent No. 5,620,683 to Tong, et al. discloses a resin comprising a random copolymer of n-alkyl acrylamide (the hydrophobic component) and acrylic acid (the hydrophilic component). Although the polymers are said to be suited to use in low VOC formulations, such polymers tend to be insoluble in water. Rather, they form a slurry in water and ethanol blends. Only upon adding the liquefied propellant gas, such as dimethyl ether, to the aerosol cans, does the resin dissolve. Preparing a slurry and pumping it into the aerosol cans is impractical for most purposes. In addition, because the resin is insoluble in water, it may prove difficult to wash from the hair.

U.S. Patent No. 5,599,524 to Morawski, et al. discloses a hair spray composition in a formulation having 80% VOC's, or less. A defoaming agent is added

to a conventional hair resin to reduce surface tension and to eliminate foaming of aerosol and non-aerosol hair sprays. The composition does not provide an improvement in flaking, fly away, or humidity resistance over conventional formulations.

U.S. Patent No. 5,501,851 to Mudge, et al. discloses a random copolymer  
5 of butyl acrylate, methyl methacrylate, hydroxyethyl acrylate, and methacrylic acid for low VOC formulations. The polymer is dispersed in an emulsion to render it later removable with a shampoo.

The present invention provides for new and improved block/branched  
10 copolymers and hair treatment compositions incorporating the copolymers, which overcome the above-referenced problems, and others.

#### Summary of the Invention

The present invention has resulted from the discovery that a block  
15 copolymer for use in hair styling compositions can be prepared from ethylenically unsaturated monomers utilizing a polyfunctional organic monomer, having at least two functional groups, or chain extender monomer, where the reactivity of the functional groups is substantially different to produce an AB block copolymer. The polyfunctional monomer polymerizes with a first monomer or mixture of monomers through the functional group having the greater reactivity to form a first or A block. A second  
20 monomer or mixture of monomers contains at least one carboxylic acid group and copolymerizes with the less reactive functional group of the chain extender monomer to form a second, or B, block. The result is a block copolymer in which the A-block is more hydrophobic than the B-block so that the copolymer has both hydrophobic and hydrophilic blocks and has a plurality of glass transition temperatures and which  
25 provides exceptional utility as a hair styling composition.

In accordance with another aspect of the present invention, a hair styling  
composition includes about 1 to 20 weight percent of a block copolymer in accordance  
with the present invention, together with 20 to 99 weight percent of water and 0 to 80  
weight percent of an organic solvent. In addition, a method of preparing a hair styling  
30 composition is provided. The method includes preparing an AB block copolymer having hydrophobic and hydrophilic blocks by polymerizing a polyfunctional organic monomer(s) which has at least two functional groups with a first ethylenically

unsaturated monomer(s) to form an A-Block, and then polymerizing a second ethylenically unsaturated monomer(s) containing at least one carboxylic acid group with the A-block to form a B-block and a copolymer having hydrophobic and hydrophilic blocks. To prepare hair styling compositions 1-20 % wt. of the block copolymer is combined with 20-97 % wt. of water, 0 to 80 % wt. of organic solvent, 0 to 5 % wt. surfactant and conditioning agents, 0 to 1% wt. fragrance, and other ancillary agents.

One advantage of the present invention is that it enables hair styling compositions to be prepared with optimal performance properties, such as style retention at high humidity, tack, hardness, flaking, washability from the hair and other subjective performance attributes.

Another advantage of the present invention is that the copolymers provided can be incorporated into hydro-alcoholic hair styling formulations to meet reduced VOC, regulations and they are effective as styling agents in a wide variety of hair styling formulations, including aerosol sprays, mousses, spritzes, gels, setting lotions, and the like.

Yet another advantage of the present invention is that the copolymers can be used for a variety of other applications where a coating composition or film forming polymer would be employed which can benefit from the fact that the block copolymer has hydrophobic and hydrophilic blocks.

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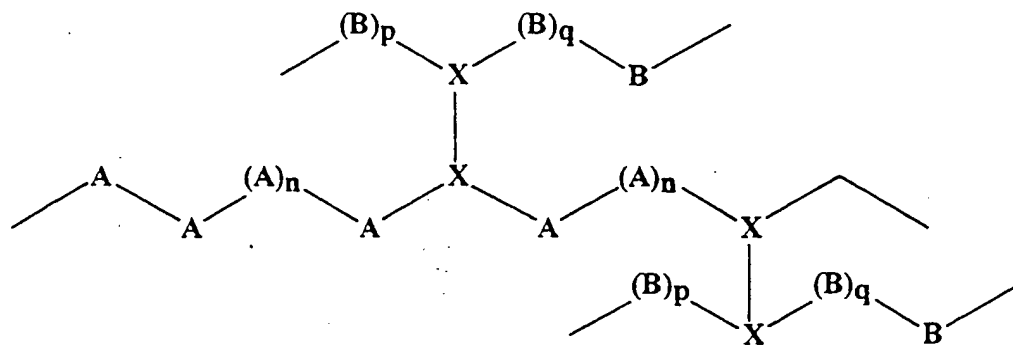
#### Detailed Description of the Preferred Embodiments

**A-Block**/branched copolymer having two or more distinct glass transition temperatures ( $T_g$ ) can be tailored to provide the desired properties in a hair care composition. The copolymer has a block structure, consisting essentially of a hard, hydrophilic block, which contributes to a high  $T_g$ , and a soft, more hydrophobic block, which contributes to a low  $T_g$ . The hydrophobic block forms the A-Block of the copolymer, while the hydrophilic block forms the B-Block. The hydrophilic B-Block and hydrophobic A-Block contribute different properties to the overall copolymer. The soft, low- $T_g$  hydrophobic A-Block contributes properties such as the formation of a uniform, clear film on the surface of the hair, providing high humidity resistance for durable hair style retention, conditioning and detangling the hair while wet, conferring the dried hair with a soft feel to the touch, adherence to the hair without flaking,

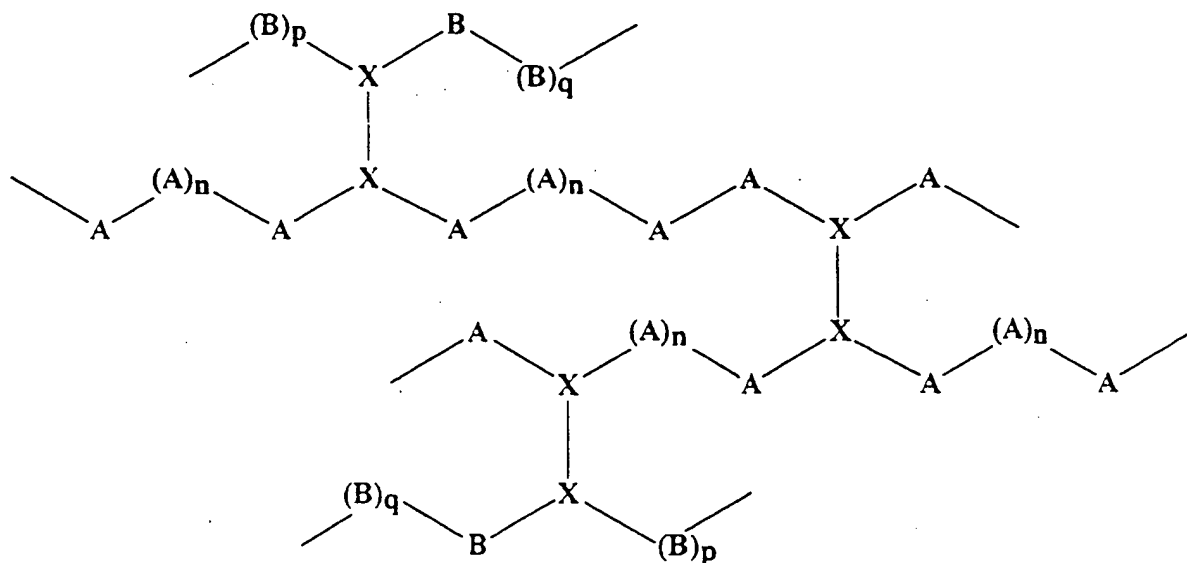
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reshaping of the hair by application of a curling iron. The hard, high- $T_g$ , hydrophilic block provides the copolymer with benefits such as ease of dispersion of the copolymer in water, alcohol, or mixtures thereof, provision of a firm hold when applied to the hair, ease of washability from the hair, and detangling of the wet hair with a comb. These properties can be tailored by varying the composition and length of the blocks. For hair styling and fixing compositions, the hydrophobic A-Block is preferably a polyacrylate, while the hydrophilic branches are preferably formed from methacrylic acids or other polymer-forming carboxylic acids.

The general structure of the copolymer of this invention can be represented by the following two structures:



Structure 1.



Structure 2.

where A represents the monomer or monomers of the first block, referred to herein as the "A-Block," and B represents the monomer or monomers of the second block, referred to herein as the "B-Block." X represents a chain branching agent or a multifunctional monomer used to link the A and B-Blocks. In these structures, n represents the degree of polymerization of the A-Block, i.e., the number of monomer units in the A-Block. Its value is typically larger than 100. The letters q and p represent the degree of polymerization of the B-Block, i.e. the number of monomer units in the B-Block. Their added value is typically larger than 100. Either q or p can take the value of zero but not both at the same time. The straight line between two monomers (A—A) represents a covalent chemical bond.

The copolymers of this invention, as represented in Structures 1 and 2 above, are blocky and may form three-dimensional networks. The existence of the two blocks was confirmed by conducting differential scanning calorimetry on dry polymer samples. It is well known that the presence of two or more transition temperatures,  $T_g$ 's, is a clear indication of the blocky character of the copolymers, see. e.g., "Contemporary Polymer Chemistry" 2<sup>nd</sup>. Edition by H. Allcock and F. Lampe, Ch. 17, Prentice Hall Publishers, 1990. The A-Blocks and the B-Blocks are covalently or chemically attached through the chain branching agent X.

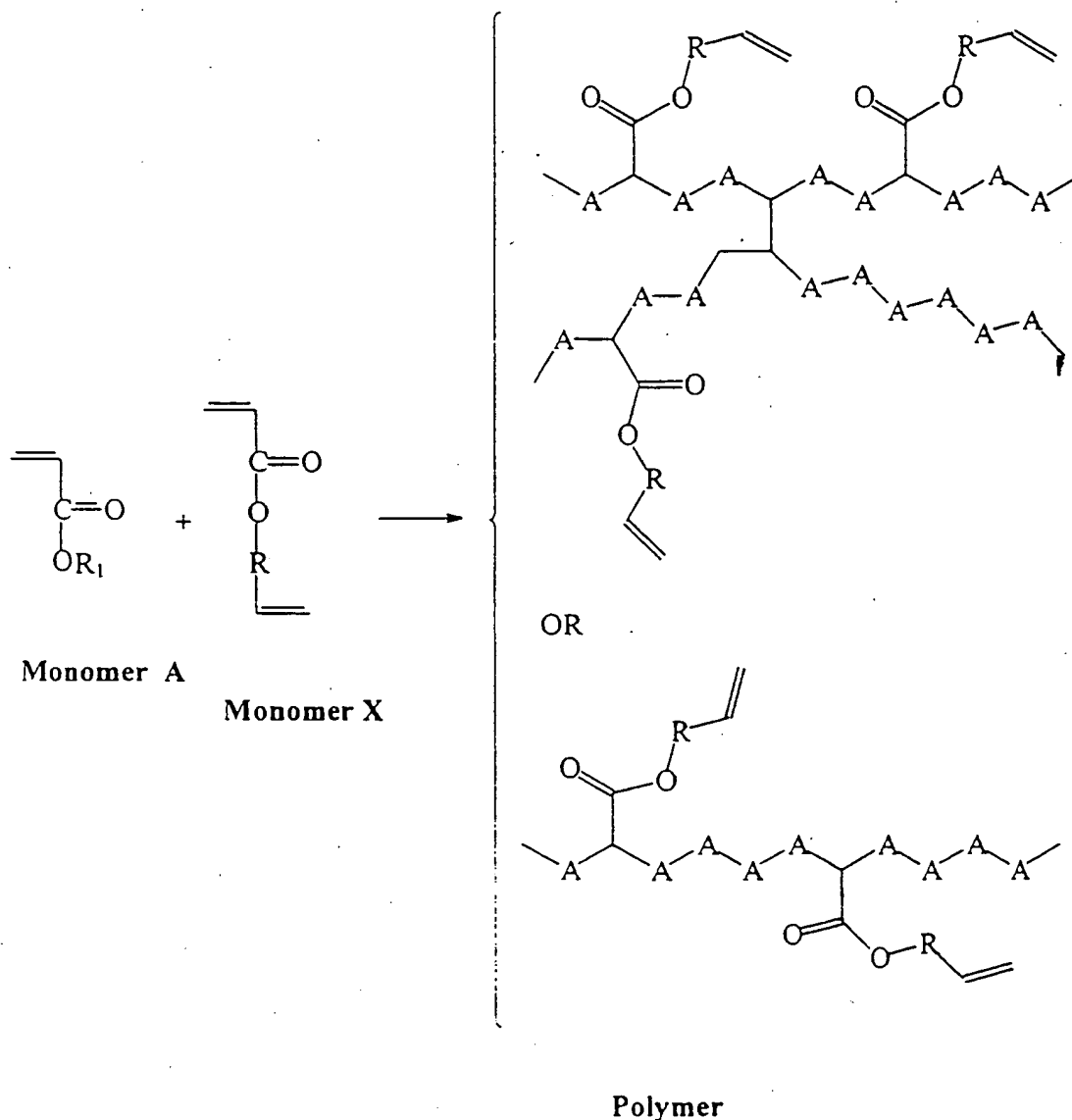
The average molecular weight of the copolymer can reach up to 1,000,000. The preferred molecular weight is in the 20,000 to 250,000 range. The preferred molecular weight of the A-Block is in the range of 10,000 to 150,000, whereas the preferred molecular weight of the B-Block is in the range of 1,000 to 50,000.

Therefore, the copolymers of this invention attain their unique hair styling and fixing properties attributes due to a combination of soft and hard blocks. The A-Block is a soft more hydrophobic block, with low  $T_g$ , and the B-Block is a hard, hydrophilic high  $T_g$  block. In addition, the length and composition of the blocks of the polymer can be varied to improve specific performance needs. In particular, the copolymers of this invention are designed to provide long lasting hair style retention at high humidity, natural feel, good hair combing, reduced flaking, no build up, and good hair styling and restyling. They are good film formers, water and alcohol soluble or dispersible and washable with water and shampoo.



To form the copolymer of the present invention, a two-step reaction process is used. This polymerization can be performed in a single reactor without having to isolate either the A or B-Block as an intermediate. The first step yields the **A-Block** portion of the copolymer, while the second step adds on the **B-Blocks** to form the resulting copolymer. In the first step, the monomers **A**, such as an acrylate, methacrylate, or a vinyl monomer, is copolymerized with a relatively small amount of the second chain extender monomer **X**. The monomer **X** has two or more polymerizable functional groups. The reactivity of the functional groups is such that the first monomer **A** reacts preferentially with a first functional group leaving the second functional group predominately unreacted. A preferred monomer **X** has both allyl and acrylate and methacrylate groups, for example, allyl methacrylate. The acrylate and methacrylate groups polymerize faster, due to its higher reactivity relative to the allyl groups. In the first step, the allyl groups remain predominantly unreacted.

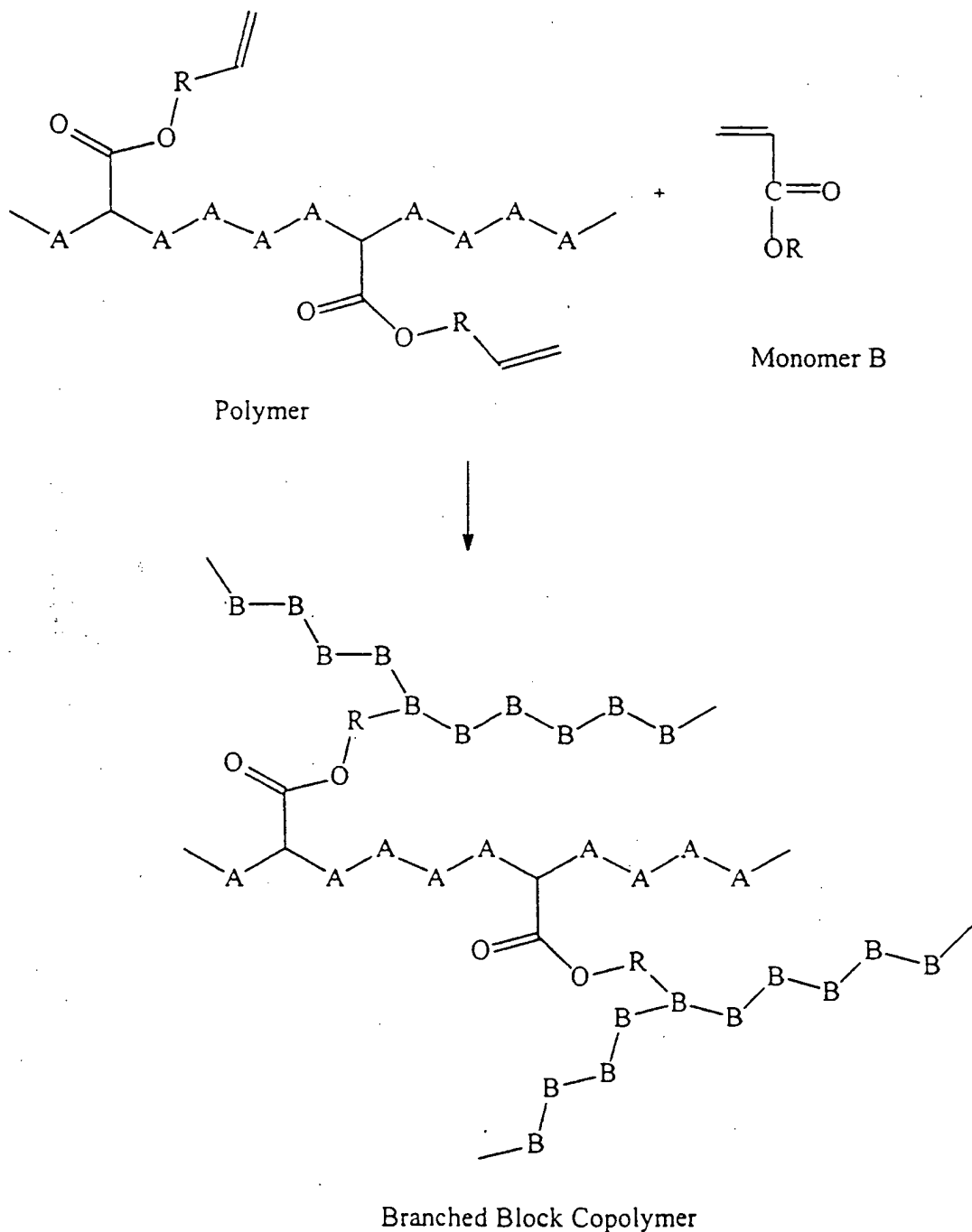
The first and second monomers react to produce a polymer. The polymer may be a linear or a branched polyacrylate with allyl functional side arms.



5 where **R** and **R**<sub>1</sub> are chemical groups described later and where **A** represents the incorporated monomer **A**. While two structures for the polymer have been shown, it should be understood that combinations of the two structures, including linear and branched portions, may be formed.

10 In the second step, monomers **B**, such as an acrylic or methacrylic acrylate or methacrylate monomer, is added and reacted with the slower reacting, second

functional groups of the polymer to obtain a three-dimensional branched and blocky copolymer.



where R<sub>2</sub> is preferably an alkyl group and B represents the incorporated monomer B.

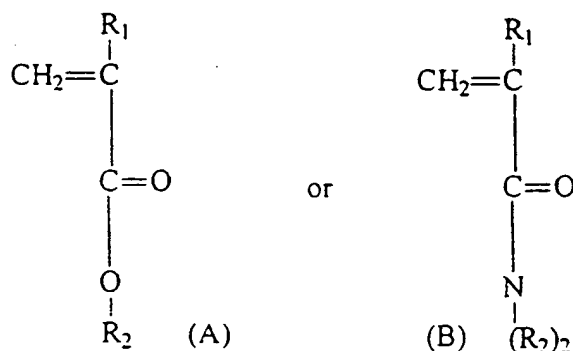
- 5 The copolymer thus has a backbone, primarily derived from the monomers A and branches derived primarily from the monomer B.

This method is not limited to preparing the hydrophobic monomer Block first with the multifunctional monomer, then preparing the hydrophilic B-Block. The order of addition can be changed. This is obvious to those familiar with the art of polymerization.

5           The **B-Block** of the copolymer is a hydrophilic block, while the **A-Block** is more hydrophobic than the **B-Block**. The hydrophobicity of the **A-Block** can be tailored to suit specific performance by incorporating hydrophilic monomers such as where the hydrophilic monomers is less than 60 % mol.

10           Suitable hydrophobic monomers A include those which are a) water insoluble, that is, less than 0.2 weight percent of the hydrophobic monomer will dissolve in one hundred weight parts water, and b) are ethylenically unsaturated compounds.

The hydrophobic monomers A preferably have at least 2 to 30 carbon atoms and are most preferably pendant organic groups such as:



15           where  $R_1 = -H, -CH_3, -CH_2CH_3$ , and  $R_2$  is an aliphatic hydrocarbon group having at least two carbons, such as  $C_2$  to  $C_{20}$  alkyls and cycloalkyls; polynuclear aromatic hydrocarbon groups such as naphthyls; alkylaryls wherein the alkyl has one or more carbons, preferably 4 to 8 carbons; haloalkyls of 4 or more carbons, preferably perfluoroalkyls; polyalkyleneoxy groups wherein alkylene is propylene or higher alkylene and there is at least 1 alkyleneoxy unit per hydrophobic moiety. Exemplary hydrophobic monomers  
20           include the higher alkyl esters of  $\alpha, \beta$ -ethylenically unsaturated carboxylic acids, such as methyl acrylate, methyl methacrylate, butyl acrylate, ethyl acrylate, octyl acrylate, dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, octadecyl acrylate, octadecyl methacrylate,  
25           ethyl half ester of maleic anhydride, diethyl maleate, and other alkyl esters derived from

the reactions of alkanols having from 2 to 20, preferably from 2 to 8, carbon atoms with ethylenically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, itaconic acid and aconitic acid; alkylaryl esters of ethylenically unsaturated carboxylic acids such as nonyl  $\alpha$ -phenyl acrylate, nonyl- $\alpha$ -phenyl methacrylate, dodecyl- $\alpha$ -phenyl acrylate and dodecyl- $\alpha$ -phenyl methacrylate; N-alkyl, ethylenically unsaturated amides such as N-butyl acrylamide, T-butyl acrylamide, octyl acrylamide, N-octadecyl arylamide; N-octadecyl methacrylamide, N,N-dioctyl acrylamide and similar derivatives thereof;  $\alpha$ -olefins such as octene-1, decene-1, dodecene-1 and hexadecene-1; vinyl alkylates wherein alkyl has at least 8 carbons such as vinyl laurate and vinyl stearate; vinyl alkyl ethers such as dodecyl vinyl ether and hexadecyl vinyl ether; N-vinyl amides such as N-vinyl lauramide and N-vinyl stearamide; and ar-alkylstyrenes such as t-butyl styrene.

Other suitable monomers A include N-substituted acrylamides or methacrylamides, substituted with alkyl radicals containing from 2 to 12 carbon atoms. Among the applicable acrylamides and methacrylamides are included N-ethyl acrylamide, N-tertiary-octyl acrylamide, N-decyl acrylamide, N-dodecyl acrylamide, as well as the corresponding methacrylamides.

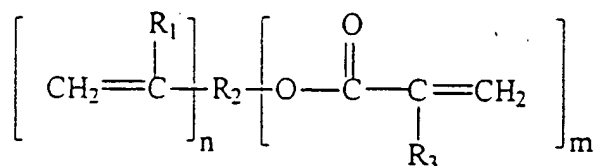
Of the foregoing hydrophobic monomers, the alkyl esters of acrylic acid, methacrylic acid, N-alkyl acrylamides, and N-alkyl methacrylamides, wherein alkyl has from 2 to 8 carbon atoms, and the alkyl styrenes, wherein alkyl has from 4 to 8 carbons, such as t-butyl, are preferred. A particularly preferred monomer A is n-butyl acrylate, ethyl acrylate and 2-ethyl hexyl acrylate.

The chain branching monomers X used in formulating the copolymer:

- a) should be multifunctional, i.e., should have at least two reactive, polymerizable, unsaturated functional groups,
- b) should contain a suitable combination of two or more unsaturated functional groups such as vinyl, allyl, acrylate, methacrylate in the same molecule.

Preferred chain branching monomers are those containing a combination of fast and slow reacting unsaturated groups. The fast reacting group is preferentially incorporated in the polymer backbone during the first step, whereas the slow reacting group reacts preferably in the second step.

The structure of the chain branching agent can be of the following type:



5 where  $n, m = 1$  to  $4$ ,  $m + n \geq 2$

$\text{R}_1, \text{R}_3 = \text{H}, \text{Alkyl}$

$\text{R}_2 = \text{alkyl}, \text{cycloalkyl}, \text{aryl},$

$-(\text{CH}_2-\text{CH}_2-\text{O})_p-$  where  $p = 1$  to  $50$ ,

$-(\text{CH}_2(\text{CH}_3)-\text{CH}_2-\text{O})_p-$  where  $p = 1$  to  $50$ ,

10 amido, ester, polyamido, polyester.

The reactivity of one of the functional groups should be relatively lower than the reactivity of the other. Table 1 below shows the reactivity ratios,  $r_1$  and  $r_2$ , for allyl, acrylic and methacrylic functional groups; as defined in the Polymer Handbook, by H. Immergut and J. Brandrup, 3<sup>rd</sup> Edition, Interscience, 1989. It can be seen that the allyl groups react 3 to 10 times slower than the other groups.

**Table 1 Reactivities of Functional Groups**

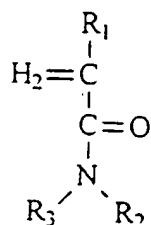
Fast Monomer/Slow Monomer	$r_1$	$r_2$
Acrylic Acid/Allyl Acetate	0.500	0.061
Methacrylic Acid/Allyl Acetate	1.129	0.066
Ethyl Acrylate/Allyl Acetate	0.600	0.165
Methyl Methacrylate/Allyl Acetate	0.383	0.136
n-Butyl acrylate/Allyl Acetate	0.427	0.199

20 Other multifunctional branching agents can also be used. Their selection should be based on the relative reactivity of their polymerizable groups. If the reactivity of the functional groups is substantially similar, then gelation during polymerization tends to occur. The polymer form is then difficult to remove from the reactor.

The monomers B are hydrophilic, or water-soluble monomers which are sufficiently water soluble to form at least a ten-weight percent solution when dissolved in

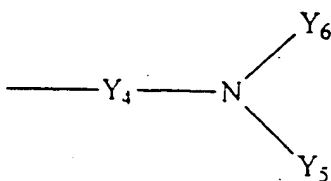
water and readily undergo additional polymerization to form polymers which are water soluble. The monomers **B** preferably contain at least one available carboxylic acid group.

Exemplary hydrophilic monomers **B** include ethylenically unsaturated amides with chemical structure:

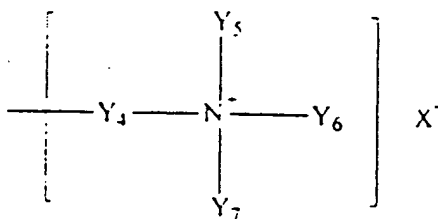


where  $R_1$  is -H, -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, branched or linear alkyl, aryl, or cycloalkyl;

$R_2$  and  $R_3$  are -H, -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, branched or linear alkyl, aryl, or cycloalkyl; acid or salt functional, such as -SO<sub>3</sub>H, -SO<sub>3</sub> M (where M = metal), or combinations thereof;



amino functional such as:



or quaternized as:

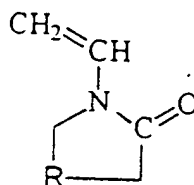
where  $Y_4$ ,  $Y_5$ ,  $Y_6$ ,  $Y_7$  are -H, -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, branched or linear alkyl, aryl, cycloalkyl, or combinations thereof.

$X^-$  = an acid radical such as chloride, bromide, sulfate, sulfonate, phosphate, methyl or ethyl sulfonate, phosphate.

Examples include acrylamide, methacrylamide and fumaramide, and their N-substituted derivatives such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS), N-(dimethylaminomethyl)acrylamide as well as N-(trimethylammonium-

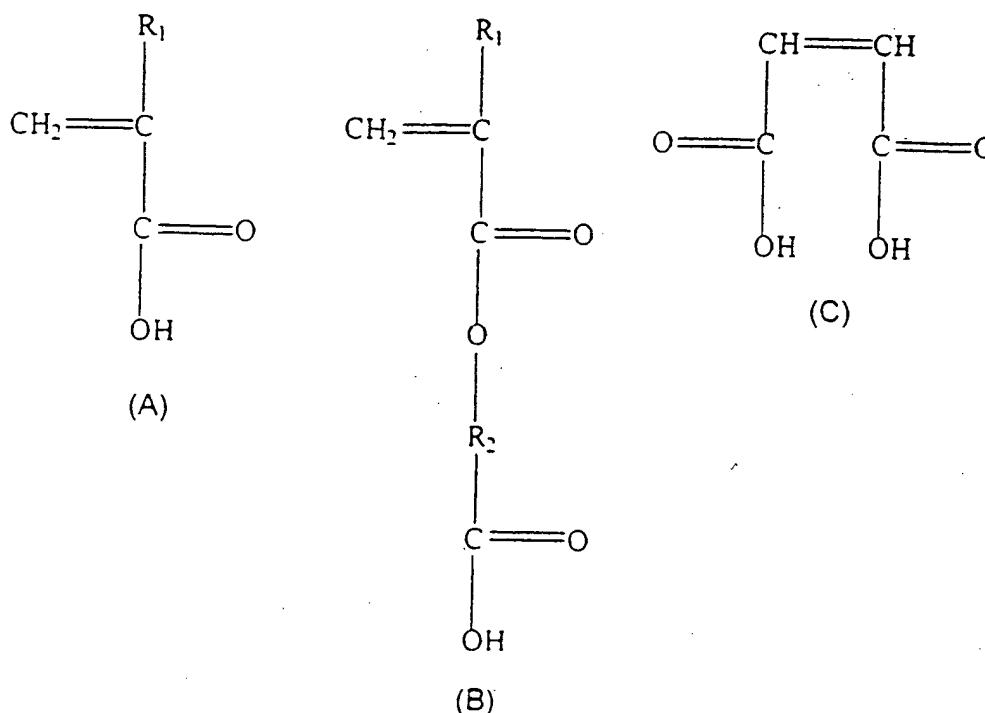
methyl)acrylamide chloride and N-(trimethylammoniumpropyl)-methacrylamide chloride.

Other ethylenically unsaturated water soluble heterocyclic amides with chemical structure:



where R is an alkylene group such as  $-(CH_2)_n$ , where  $n = 1$  to 4. Examples include vinyl pyrrolidone ( $n=1$ ), vinyl caprolactam ( $n=2$ ).

Other suitable water soluble monomers include ethylenically unsaturated carboxylic acids with general structure:

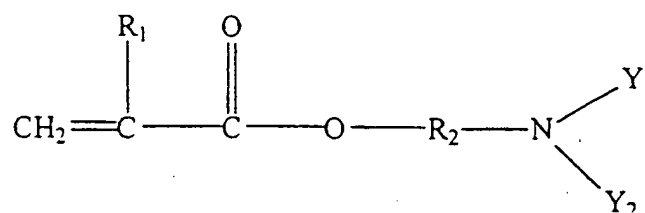


where  $R_1 = -H, -CH_3, -CH_2CH_3$

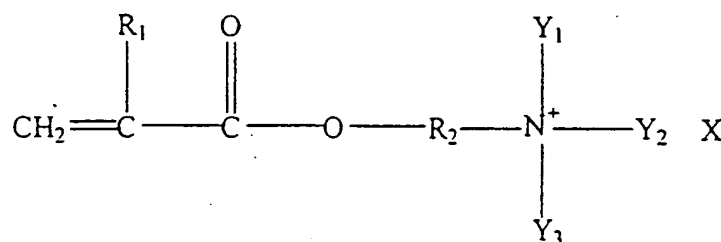
$R_2 = -(CH_2)_n$ , where  $n = 1$  to 40's, linear or branched alkyl; cycloalkyl; aryl;  
polyethylene oxide such as  $-(CH_2-CH_2-O)_p-$  where  $p = 1$  to 50;  
polypropylene oxide such as  $-(CH_2(CH_3)-CH_2-O)_p-$  where  $p = 1$  to 50.



Examples include acrylic acid, methacrylic acid, maleic acid, itaconic acid and fumaric acid, vinylaryl sulfonates such as vinylbenzyl sulfonate as well as the salts of the foregoing monomers: ethylenically unsaturated quaternary ammonium compounds such as vinylbenzyl trimethyl ammonium chloride, sulfoalkyl esters of unsaturated carboxylic acids such as 2-sulfoethyl methacrylate, and aminoalkyl esters of unsaturated carboxylic acids such as:



or their quaternized salts:



where  $\text{R}_1 = -\text{H}, -\text{CH}_3, -\text{CH}_2\text{CH}_3$ ;

$\text{R}_2 = -[\text{CH}_2-]_n$ , where  $n = 1$  to  $40$ , linear or branched alkyl, cycloalkyl, aryl,

polyethylene oxide such as  $-(\text{CH}_2-\text{CH}_2-\text{O})_p$ - where  $p = 1$  to  $50$ ,

polypropylene oxide such as  $-(\text{CH}_2(\text{CH}_3)-\text{CH}_2-\text{O})_p$ - where  $p = 1$  to  $50$ ;

$\text{Y}_1, \text{Y}_2, \text{Y}_3 = -\text{H}, -\text{CH}_3, -\text{CH}_2\text{CH}_3$ , branched or linear alkyl, aryl, cycloalkyl, or combinations thereof;

$\text{X}^-$  = an acid radical such as chloride, bromide, sulfate, sulfonate, phosphate, methyl or ethyl sulfonate.

Examples include 2-aminoethyl methacrylate, N,N-dimethyl-aminoethyl methacrylate, N,N-dimethyl aminoethyl acrylate, 2-tert-butyl aminoethyl methacrylate, 2-trimethylammonium ethylmethacrylate chloride, 2-trimethylammonium ethylacrylate chloride, vinyl amines, such as vinyl pyridine and vinyl morpholine, diallyl amines and diallyl ammonium compounds, such as diallyl dimethyl ammonium chloride.

If monomers **B** are acidic, they make it possible for the resultant copolymer to be neutralized by reaction with an appropriate base so that the copolymer may exhibit a desirable level of water solubility. For example, the copolymer may be neutralized prior to being incorporated into an ultimate hair styling composition, allowing the composition to be removed from the hair simply by washing with water. Alternatively, if the copolymers are not pre-neutralized in this manner, removal may still be readily effected by application of an aqueous alkaline solution, such as soap in water.

The exact ratio of the monomers **A** and **B** is not critical to solubility. Copolymers with a high proportion of the hydrophobic **A-Block** can be dissolved in water by adjusting the pH.

In order to modify or enhance selected properties of the copolymer, for example, resistance to humidity, washability, and the like, the monomers **A** and **B** may be single monomers, or a combination of two or more monomers.

As for the actual preparation of the copolymer, any of the usual acrylate polymerization methods known in the art, such as solvent, suspension, emulsion, and inverse emulsion polymerization methods may be employed. In one preferred method of preparation of the copolymer, the monomers **A**, **B**, and **X** are reacted together in a suitable solvent. A free radical initiator is added in small quantities.

Suitable free radical initiators include azo- and peroxo-type initiators. Examples of azo-initiators are azobis-dimethylvaleronitrile, azobis-isobutyronitrile, azobis-methylbutyronitrile and others sold by DuPont, Wilmington, DE under the trade name VAZO and by WAKO Pure Chemical Industries, Richmond, VA under the trade name of V-40 to V501. Examples of peroxo initiators include di-T butyl peroxide, T-butyl cumyl peroxide, T-butyl peroxy-pivalate, lauryl peroxide, cumene hydroperoxide, ethyl hexyl peroxodicarbonate, diisopropyl peroxydicarbonate, 4-(t-butylperoxylperoxy-carbonyl)-3-hexyl-6-7-(t-butylperoxycarbonyl)heptyl cyclohexene (4-TBPCH), cumene hydroperoxide and t-butyl peroxyneodecanoate, t-butyl hydroperoxide, benzoyl peroxide and other organic peroxides sold by Elf Atochem North America, Inc., Philadelphia, PA, under the trade names of Lupersol, Luperco, Lucidol and Luperox.

The initiator is preferably added at about 0.005 mole percent to 1 mole percent of the total monomer composition. Preferred initiators are di-T-butyl peroxide, T-butyl cumyl peroxide, T-butyl peroxy-pivalate, lauryl peroxide, cumene hydroperoxide,

ethyl hexyl peroxodicarbonate, diisopropyl peroxydicarbonate, 4-(t-butylperoxylperoxy-carbonyl)-3-hexyl-6-7-(t-butylperoxycarbonyl) heptyl cyclohexene, cumene hydroperoxide and t-butyl peroxyneodecanoate, t-butyl hydroperoxide, benzoyl peroxide and combinations thereof.

5           The polymerization can be carried in an variety of solvents, such alcohols, ethers, esters, aromatic solvents, glycols, glycol ethers, and glycol esters. Preferred solvents include ethyl alcohol, isopropyl alcohol, t-butyl alcohol, ethyl acetate, methyl acetate, butyl acetate, benzene, toluene, and methylene chloride. These solvents can be used also in combination with hydrocarbon solvents such as hexane, cyclohexane,  
10       mineral spirits, and the like. One preferred solvent is an isopropyl alcohol and water mixture.

          Preferably, a reaction vessel, containing the solvent is heated to a suitable polymerization temperature. The monomers **A**, **B**, and **X** are metered, as a mixture, into the reaction vessel, over a period of several hours. Optionally, the mixture of monomers  
15       is varied throughout the reaction period. The initiator, dissolved in an additional portion of the solvent, is simultaneously metered into the reaction vessel.

          The resulting copolymer can be dried and ground into a powder, or used directly from solution.

          The weight of each of the monomers in the mixture can vary, depending  
20       on the desired properties of the copolymer. In one preferred embodiment, the monomer **A** for A-Block comprises from about 28 to about 60% by weight of the mixture of monomers, the chain extender monomer **X** comprises from about 1 to about 1.5 by weight of the mixture, and the monomer **B** for B-Block comprises from about 38 to about 69% by weight of the mixture.

25           The copolymers are suitable additives for the formulation of hair fixative formulations, such as aerosol and non-aerosol hair spray, spritz, gel, spray gel, mousse, styling creams, hair relaxers, and the like. The copolymer is compatible with dyes and pigments suitable to prepare colored hair fixatives. Since the copolymers are soluble in water and alcohol mixtures, they are suitable for the formulation of reduced volatile  
30       organic compounds (VOC) fixative formulations. The copolymers can be used to prepare 80%, 55%, 30%, or less VOC, and alcohol free formulations.

The copolymer is also suitable for the preparation of shampoos, conditioners, rinses, liquid soap, soap bars, detergents, cleaners, room deodorizers, and the like.

5 The copolymers are also suitable additives for the formulation of hair and skin creams, lotions, pomades, and ointments; topical medicated creams, skin protective films, hair depilatories, hair shaving creams, hand and body lotions, mascaras, sunscreens, and such.

10 The copolymer also finds application as additive in nail care formulations such as water-based nail polish, nail repair, nail protection, and the like because it is a film forming polymer which is removable due to the polymer having both hydrophobic and hydrophilic group.

15 The copolymer can also be used advantageously in the formulation of pharmaceutical formulations such as creams, pomades, gels, tooth paste, tablets, gel capsules, enema fluids, vomitives, suppositories, foamed anti-fungal preparations, drug delivery compositions to deliver transdermally active ingredients to or through the skin, ocular fluids, anti-acne formulations, topical analgesics, and the like.

20 The block/branched copolymers can be used in a host of applications where the presence of polymeric blocks with different properties is a useful property. They can be used as additives in cosmetic applications, body implants, coatings for catheters, cannulae, antiperspirant and deodorant formulations, coating for medical devices, gloves, removable protective coatings, wound dressings, etc. They can be used in the formulation of inks, protective washable coatings for textiles, fabrics, metal strippers, and the like.

25 In particular, the polymers of this invention are designed to provide a combination of long lasting hair style retention at high humidity, natural feel, good hair combing, reduced flaking, no build up, and good hair stylability and restyling. They are good film formers, washable with water and shampoo.

30 Formulations incorporating the copolymers may be delivered from aqueous or hydro-alcoholic solutions, dispersions, or emulsions. The copolymers can be dissolved in water, water-ethanol or water-solvent mixtures by dispersing the copolymer in the solvent and adjusting the pH with an organic or inorganic base between pH3 and

pH12. A preferred pH is 5.0 to 9.0. Within this pH range, water clear solutions of the copolymer can be prepared.

In preparing hair styling compositions which incorporate the copolymer, the copolymer, either in powdered or liquid form, is combined with a solvent system, or with a solvent/propellant system. Preferably, the copolymer comprises between about 0.01-20% by weight of the total weight of the composition, more preferably between 0.5-10% by weight. The solvent system preferably includes water and an organic solvent. Suitable organic solvents include alcohols, glycols and ketones, such as ethanol, isopropanol, acetone, dioxymethane, or methyl ethyl ketone, propylene glycol, hexylene glycol, and butylene glycol. For low VOC compositions, the solvent system preferably includes at least 20-50 weight percent water, and optionally up to 100% water. Preferably not more than about 25 weight percent of the organic solvent is used.

The hair styling compositions may be in the form of an aerosol or non-aerosol spray, a mousse, gel, or hair setting lotion. The compositions may contain up to 60 weight percent, preferably up to 35 weight percent, of liquified gases. Typical propellants include ethers, compressed gases, halogenated hydrocarbons and hydrocarbons. Exemplary propellants are dimethyl ether, compressed nitrogen, air or carbon dioxide, propane, butane, and 1,1 difluoroethane. Optionally, the solvent acts as the propellant.

The compositions may further include other materials or formulation additives, such as fragrances, preservatives, dyes and other colorants, plasticizers, emulsifiers, conditioners, neutralizers, glossifiers, lubricants, penetrants, UV absorbers, and the like. Mousses, according to the present invention, may further comprise from about 0.25 to 6 weight percent, preferably 0.25 to 3 weight percent, of an emulsifier. The emulsifier may be nonionic, cationic, anionic, or amphoteric.

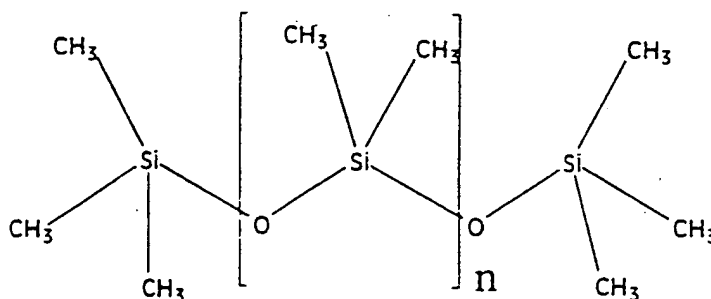
#### Formulation Additives

Examples of additives are used in the formulation of hair, skin and nail products, include the following:

Conditioning Agents: In accordance with one important embodiment of the present invention, the composition of the present invention also includes from about 0.1% to

about 10%, particularly about 0.5% to about 10%, and preferably from about 1.0% to about 5.0%, by weight of a non-volatile silicone compound or other conditioning agent(s), preferably a water-insoluble, emulsifiable conditioning agent. The preferred non-volatile silicone compound is a polydimethylsiloxane compound, such as a mixture, in about a 3:1 weight ratio, of a low molecular weight polydimethylsiloxane fluid and a higher molecular weight polydimethylsiloxane gum. The non-volatile polydimethylsiloxane compound is added to the composition of the present invention in an amount sufficient to provide improved combing and improved feel (softness) to the hair. As referred to herein, "silicone gums" are those nonfunctional siloxanes having a viscosity of from about 5 to about 600,000 centistokes at 25 °C.

The so-called rigid silicones, as described in U.S. Pat. No. 4,902,499, herein incorporated by reference, having a viscosity above 600,000 centistokes at 20 °C., e.g. 700,000 centistokes plus, and a weight average molecular weight of at least about



500,000 also are useful in accordance with the present invention. Preferred silicone gums include linear and branched polydimethylsiloxanes. Silicone gums useful in compositions of the present invention are available from a variety of commercial sources, including General Electric Company, Dow Corning and B.F. Goodrich.

Another particularly suitable conditioning agent that can be included in the composition of the present invention is a volatile hydrocarbon, such as a hydrocarbon including from about 10 to about 30 carbon atoms, that has sufficient volatility to slowly volatilize from the hair after application of the aerosol or non-aerosol styling aid composition. The volatile hydrocarbons provide essentially the same benefits as the silicone conditioning agents. The preferred volatile hydrocarbon compound is an aliphatic hydrocarbon

including from about 12 to about 24 carbon atoms, and having a boiling point in the range of from about 100°C to about 300°C. Examples of volatile hydrocarbons useful in the composition of the present invention are the commercially-available compounds PERMETHYL 99A and PERMETHYL 101A, available from Permethyl Corporation, Frazer, Pennsylvania. A volatile hydrocarbon compound is useful in the composition of the present invention either alone, in combination with another volatile hydrocarbon, or in combination with a volatile silicone. Examples of other suitable water-insoluble conditioning agents that can be incorporated into the aerosol or non-aerosol aqueous styling aid composition of the present invention include the following: polysiloxane polyether copolymers; polysiloxane polydimethyl dimethylammonium acetate copolymers; acetylated lanolin alcohols; dimethyl dialkyl ammonium chlorides; modified alkyl dimethyl benzyl ammonium chlorides; lauryl dimethylamine oxide; stearyl dimethyl benzyl ammonium chloride; a lanolin-derived extract of sterol on sterol esters; lanolin alcohol concentrate; an isopropyl ester of lanolin fatty acids; sulfur rich amino acid concentrates; isopropyl ester of lanolin fatty acids; stearyl dimethyl benzyl ammonium chloride; cetyl trimethyl ammonium chloride; oleyl dimethyl benzyl ammonium chloride; oleyl alcohol; stearyl alcohol; stearyl dimethyl benzyl ammonium chloride; stearamidopropyl dimethyl myristyl acetate; a polyol fatty acid; a fatty amido amine; guar hydroxypropyltrimonium chloride; cetyl/stearyl alcohol; quaternized protein; keratin protein derivatives: isostearamidopropyl dimethylamine; stearamidopropyl dimethylamine; cetrimonium bromide; myrtrimonium bromide; stearalkonium chloride; cetyl trimethyl ammonium chloride; laurylpyridinium chloride; tris(oligoxyethyl)alkyl ammonium phosphate; an aminofunctional silicone; lapyrium chloride; isopropyl ester of lanolic acids: ethoxylated (30) castor oil; acetylated lanolin alcohol; fatty alcohol fraction of lanolin: a mineral oil and lanolin alcohol mixture; high molecular weight esters of lanolin: quaternium-75; vinylpyrrolidone/dimethylaminoethylmethacrylate copolymer; alkyl trimethyl ammonium chloride; 5 mole ethylene oxide adduct of soya sterol; 10 mole ethylene oxide adduct of soya sterol; stearic acid ester of ethoxylated (20 mole) methyl glucoside; sodium salt of poly-hydroxycarboxylic acid; hydroxylated lanolin: cocamidopropyl dimethylamine lactate; cocamidopropyl dimethylamine propionate; cocamidopropyl morpholine lactate; isostearamidopropyl dimethylamine lactate: isostearamidopropyl

morpholine lactate; oleamidopropyl dimethylamine lactate; linoleamidopropyl  
 dimethylamine lactate; stearamidopropyl dimethylamine lactate, ethylene glycol  
 monostearate and propylene glycol mixture; stearamidopropyl dimethylamine lactate;  
 acetamide MEA; lactamide MEA; stearamide MEA; behenalkonium chloride; behenyl  
 5 trimethyl ammonium methosulfate and cetearyl alcohol mixture; cetearyl alcohol;  
 isostearamidopropalkonium chloride; linoleamidopropalkonium chloride; oleyl dimethyl  
 benzyl ammonium chloride; tallow imidazolinum methosulfate; stearyl dimethyl benzyl  
 ammonium chloride; stearyl trimonium methosulfate; mixed ethoxylated and  
 propoxylated long chain alcohols; stearamidopropyl dimethylamine lactate; polonitamine  
 10 oxide; oleamine oxide; stearamine oxide; soya ethyldimonium ethosulfate;  
 hydroxypropyl bislauryl-dimonium chloride; hydroxypropyl biscetyl-dimonium chloride;  
 hydroxypropyl bisstearyl dimonium chloride; hydroxypropyl bisbehenyl dimonium  
 chloride; ricinoleamidopropyl ethyldimonium ethosulfate; olealkonium chloride;  
 stearalkonium chloride; N-(3-isostearamidopropyl)-N,N-dimethyl amino glycolate;  
 15 N-(3-isostearamidopropyl)-N,N dimethyl amino gluconate; hydrolyzed animal keratin;  
 ethyl hydrolyzed animal keratin; stearyl ammonium chloride; stearamidoethyl  
 diethylamine; cocamidopropyl dimethylamine; lauramidopropyl dimethylamine;  
 oleamidopropyl dimethylamine; palmitamidopropyl dimethylamine; stearamidopropyl  
 dimethylamine lactate; avocado oil; sweet almond oil, grape seed oil; jojoba oil; apricot  
 20 kernel oil; sesame oil; hybrid safflower oil; wheat germ oil; cocamidoamine lactate;  
 ricinoleamido amine lactate; stearamido amine lactate; stearamido morpholine lactate;  
 isostearamido amine lactate; isostearamido morpholine lactate; wheat germamido  
 dimethylamine lactate; behenamidopropyl betaine; ricinoleamidopropyl betaine; wheat  
 germamidopropyl dimethylamine oxide; disodium isostearamido MEA sulfosuccinate;  
 25 disodium oleamide PEG-2 sulfosuccinate; disodium oleamide MEA sulfosuccinate;  
 disodium ricinoleyl MEA sulfosuccinate; disodium wheat germamido MEA  
 sulfosuccinate; disodium wheat germamido PEG-2 sulfosuccinate; stearalkonium  
 chloride; stearyl dimethyl benzyl ammonium chloride; stearamido amine; stearamido  
 morpholine; isostearamido amine; isostearamido morpholine; polyethylene glycol (400)  
 30 mono and distearates; synthetic calcium silicate; isostearic alkanolamide; ethyl esters of  
 hydrolyzed animal protein; blend of cetyl and stearyl alcohols with ethoxylated cetyl or  
 stearyl alcohols; amido amines; polyamido amines; palmityl amido betaine; propoxylated



(1-20 moles) lanolin alcohols; isostearamide DEA; and hydrolyzed collagen protein.

When one or more of these water-insoluble conditioning agents is included in the composition of the present invention in an amount of about 0.5% to about 10% by total weight of the composition, the composition also can include a suspending agent for the conditioning agent, in an amount of about 0.5% to about 10%, by total weight of the composition. The particular suspending agent is not critical and can be selected from any materials known to suspend water-insoluble liquids in water. Suitable suspending agents are for example, distearyl phthalamic acid; fatty acid alkanolamides; esters of polyols and sugars; polyethylene glycols; the ethoxylated or propoxylated alkylphenols; ethoxylated or propoxylated fatty alcohols; and the condensation products of ethylene oxide with long chain amides. These suspending agents, as well as numerous others not cited herein, are well known in the art and are fully described in the literature, such as McCutcheon's Detergents and Emulsifiers, 1989 Annual, published by McCutcheon Division, MC Publishing Co. A nonionic alkanolamide also is optionally included in an amount of about 0.1% to about 5% by weight in the styling aid compositions that include a conditioning agent to provide exceptionally stable emulsification of water-insoluble conditioning agents and to aid in thickening and foam stability. Other useful suspending and thickening agents can be used instead of the alkanolamides such as sodium alginate; guar gum; xanthan gum; gum arabic; cellulose derivatives, such as methylcellulose, hydroxybutylcellulose, hydroxyethylcellulose, hydroxypropylcellulose and carboxymethylcellulose; and various synthetic polymeric thickeners, such as the polyacrylic acid derivatives. Suitable alkanolamides include, but are not limited to, those known in the art of hair care formulations, such as cocamide monoethanolamide (MEA), cocamide diethanolamide (DEA), soyamide DEA, lauramide DEA, oleamide monoisopropylamide (MIPA), stearamide MEA, myristamide MEA, lauramide MEA, capramide DEA, ricinoleamide DEA, myristamide DEA, stearamide DEA, oleylamide DEA, tallowamide DEA, lauramide MIPA, tallowamide MEA, isostearamide DEA, isostearamide MEA and combinations thereof.

**Neutralizing Agents:** In certain applications such as hair and skin care compositions, it is necessary to neutralize the hydrophilic B-block of the copolymer to achieve solubility or dispersibility. Neutralization and increased solubilization are accomplished, but not

limited to, with one or more inorganic bases such as sodium hydroxide, potassium hydroxide, ammonium hydroxide and/or ammonium carbonate. Among stable organic bases are the water soluble alkanol amines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-methyl-2-amino-1-propanol (AMP),  
5 monoamino glycols, and the like, which help solubilize the polymer in water solutions. The level of neutralization required for solubilization varies for each polymer. The block copolymers become soluble in water and hydroalcoholic solutions at 20% to 100% neutralization, and at all described levels of water/alcohol/propellant solutions. The pH of these solutions usually ranges from 4 to 12. The lowest neutralization level needed to  
10 render the polymer water soluble or dispersible depends on the composition of the block polymer, and the amount of alcohol, water, and propellant.

**Aerosol Propellant Gas:** The propellant gas included in the aerosol compositions of the present invention can be any liquefiable gas conventionally used for aerosol containers.  
15 Examples of materials that are suitable for use as propellants are trichlorofluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane, monochlorodifluoromethane, trichlorotrifluoroethane, dimethyl ether, propane, n-butane and isobutane, used singly or admixed. Water-soluble gases such as dimethyl ether, carbon dioxide, and/or nitrous oxide also can be used to obtain aerosols having reduced flammability.  
20 Water-immiscible, liquified, hydrocarbon and halogenated hydrocarbon gases such as propane, butane and chlorofluorocarbons can be used advantageously to deliver the contents of the aerosol container without the dramatic pressure drops associated with other immiscible gases. Here there is no concern for the head space to be left inside the aerosol container, because the liquified gas will sit on top of the aqueous formulation and the pressure inside the container is always the vapor pressure of saturated hydrocarbon  
25 vapor. Other insoluble, compressed gases such as nitrogen, helium and fully-fluorinated oxetanes and oxepanes also are useful to deliver the compositions from aerosol containers. Other means of delivery of the above-described aqueous styling aid compositions include, pump sprayers, all forms of bag-in-can devices, in situ carbon  
30 dioxide (CO<sub>2</sub>) generator systems, compressors, and the like. The amount of the propellant gas is governed by normal factors well known in the aerosol art. For mousses, the level of propellant is generally from about 3% to about 30%, preferably from about

5% to about 15% of the total composition. If a propellant such as dimethyl ether utilizes a vapor pressure suppressant (e.g., trichlorethane or dichloromethane), for weight percentage calculations, the amount of suppressant is included as part of the propellant.

5     **Optional Additives:** The hair styling compositions also can contain a variety of other nonessential, optional components suitable for rendering such compositions more aesthetically acceptable. Such conventional optional ingredients are well known to those skilled in the art, e.g., other emulsifiers such as anionics (e.g., sodium alkyl sulfate); preservatives such as benzyl alcohol, methyl paraben, propyl paraben and  
10     imidazolidinylurea; cationic emulsifiers/conditioners such as cetyl trimethyl ammonium chloride, stearyldimethyl benzyl ammonium chloride, and di(partially-hydrogenated tallow) dimethylammonium chloride; viscosity modifiers such as a diethanolamide of a long chain fatty acid, fatty alcohols (i.e., cetearyl alcohol), sodium chloride, sodium sulfate, and ethyl alcohol; pH adjusting agents such as citric acid, succinic acid, sodium  
15     hydroxide and triethanolamine; coloring agents such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents such as hydrogen peroxide, perborate salts and persulfate salts; hair reducing agents such as thioglycolates; perfume oils; chelating agents such as ethylenediaminetetraacetic acid; and, among many other agents, polymer plasticizing agents such as glycerin and propylene glycol. These optional materials are  
20     generally used individually at a level of from about 0.01% to about 19%, preferably from about 0.5% to about 5% by weight of the total composition. The aqueous formulations of the present invention also can contain the conventional hair spray adjuvants in amounts which generally range from about 0.1 to 2% by weight and preferably about 0.75 to 1% by weight. Among the additives which can be used are plasticizers such as  
25     glycols, phthalate esters and glycerine; silicones; emollients; lubricants and penetrants such as various lanolin compounds; protein hydrolysates and other protein derivatives; ethylene adducts and polyoxyethylene cholesterol; dyes, tints and other colorants; and perfumes.

30     **Carrier Vehicle:** Polar solvents are typically used to prepared the cosmetic or hair compositions. Water, glycols and alcohols are preferably used. The optional alcohol employed in the composition is an aliphatic straight or branched chain monohydric

alcohol having 2 to 4 carbon atoms. Isopropanol and especially ethanol are preferred. The concentration of the alcohol in the composition should be less than about 40% by weight, and surprisingly can be as low as 0%, preferably 0-30% by weight and more preferably 5-20% by weight. Some alcohol, in an amount of about 2% to about 10% by weight.

In preparing the hair styling compositions of the present invention, the copolymer is optionally neutralized to the extent that from about 40 to 100 mole percent of the carboxylic groups in the copolymer are neutralized by a neutralization agent, in a solvent system wherein water is the primary solvent. At neutralizations greater than around 92%, the humidity resistance of the hair styling composition is greatly reduced.

The hair styling compositions incorporating the branched block copolymer exhibit desirable characteristics of such compositions, including long lasting hair style retention at high humidity, natural feel, good hair combing, reduced tack, reduced flaking, good stylability and restyling, no fly away, and the like.

Other applications for the polymers of the present invention would include: adhesive, metal cleaners, oil/gas well cleaners, preservative intermediate, polystyrene manufacture, surface cleaners, industrial cleaners, coatings, industrial coatings, specialty and imaging, paint stripper, printing inks, photo-resist applications, paints/latex systems, battery manufacture, reaction solvent and fiber dying, detergents, textile dye stripping, printed circuit boards, dispersants, gel former, petrochemical processing, and paper manufacture.

While not intended to limit the invention, the following examples are illustrative of the methods of preparing the copolymers and hair styling compositions, and of their unique styling properties.

#### General Method Of Preparation Of Polymers

The following method was used to prepare a variety of copolymers. A clean, dry 8 liter glass reactor was set up in a heated waterbath and fitted with a condenser and a stirring agitator. To the reactor, 1750 grams of solvent, a mixture of 80% isopropyl alcohol and 20% water, was charged and heated to reflux temperature (78-82°C). A first batch, or feed of monomers for forming the A-Block, 1200 grams of n-butyl acrylate, and 116 grams of methacrylic acid, and 20 grams of a chain extender,

allyl methacrylate, were mixed together and charged into a storage cylinder connected to the reactor by a feed line and a metering pump. 16.8 grams of an initiator, t-butyl peroxyvalate were diluted with a further 200 grams of solvent and charged to another storage cylinder also connected to the reactor by a metering pump.

5           After the reactor reached reflux temperature the polymerization was started. The first batch of monomers was fed in evenly over a one hour period and the initiator was fed in over evenly over a four hour period. After the first hour, a second batch, or feed, of monomers for forming the **B-Block**, a blend of 1053 grams of methacrylic acid and 10 grams of allyl methacrylate chain extender was fed into the reactor evenly over a two  
10   hour period. The total monomer feed time was three hours and the total initiator feed time was four hours. After all the ingredients had been added, the reactor was held at reflux temperature for another two hours before cooling to room temperature.

The resulting reaction mixture comprised 50 percent solids by weight.

The above method was used to prepare copolymers of varying  
15   compositions. The molecular weight (Mw) of the polymers was measured by gel permeation chromatography, GPC. The  $T_g$  of the polymers was measured using differential scanning calorimetry, DSC. Table 2 summarizes the quantities of the three monomers used in preparing each of the copolymers, in terms of the weight added in each of the two feed mixtures, and the total weight of monomer added in both the  
20   mixtures. The percentage solids in the reactor at the end of the reaction period is included for each of the copolymers prepared, together with the high and low glass transition temperatures of the copolymer, and the molecular weight of the copolymer.

**Key for the Examples of Polymers:**

25           In the examples, the following abbreviations will be used:

nBA	=	n-butyl acrylate
All MA	=	(chain extender) allyl methacrylate
AA	=	acrylic acid
30   MAA	=	methacrylic acid
EGDMA	=	(chain extender) ethylene glycol dimethacrylate
Lup-11	=	(initiator) t-butyl peroxyvalate (Lup-11 is short for Lupersol-11, and is available from Atochem North America, Inc.)

	IPA/H <sub>2</sub> O	=	(solvent) at 80/20 wt % mixture of isopropyl alcohol/water
	Tg 1	=	Low glass transition temperature
	Tg 2	=	High glass transition temperature
	phm	=	parts per hundred parts of monomer
5	Mw	=	weight average molecular weight

### Substantiation Examples of Block/Branched Copolymers with Two Tg

The copolymers in Examples 1 to 3 were prepared following the polymerization scheme above. The A-block was prepared using two monomers and the B-block contains only one. The A-Block is predominantly hydrophobic; the B-block is hydrophilic and ionizable. The molecular weight Mw of the polymers was measured by gel permeation chromatography, GPC. The Tg of the polymers was measured using differential scanning calorimetry, DSC.

TABLE 2

Example	Monomer Composition				Observations
		A-Block	B-Block	Total Batch	
	<i>Ingredient</i>	<i>(g)</i>	<i>(g)</i>	<i>(g)</i>	<i>phm</i>
1	AA	216.00	1944.00	2160.00	60.00
	n-BA	1386.00	0.00	1386.00	38.50
	All MA	36.00	18.00	54.00	1.50
	Lup - 11	18.00		18.00	0.50
	IPA/H <sub>2</sub> O			2400.00	66.66
2	AA	162.40	1461.60	1624.00	70.00
	n-BA	661.20	0.00	661.20	28.50
	All MA	34.80	18.00	52.80	1.50
	Lup - 11	16.24		16.24	0.50
	IPA/H <sub>2</sub> O			2400.00	66.66
3	MAA	175.00	1580.00	1755.00	48.75
	n-BA	1800.00		1800.00	50.00
	All MA	30.00	15.00	45.00	1.25
	Lup - 11			25.2	0.70
	IPA/H <sub>2</sub> O			2400.00	66.66

### Examples to Substantiate the Criticality of Using a Suitable Chain Extender

To demonstrate the blocky-structure of the polymer and the importance of using a suitable chain extender, block copolymers were prepared where the A-block was a hydrophobic, water-insoluble block and the B-block, hydrophilic and ionizable. Examples 4 and 5 were prepared in a similar manner, without and with allyl methacrylate, All MA (the chain extender monomer), respectively. The hydrophobic block of Polymer 4, after neutralizing with base at high pH, did not dissolve in water. The polymer formed a milky, phase-separated suspension. Conversely, the polymer of Example 5, which includes All MA, formed a water clear solution after neutralization with base at pH = 7.16.

TABLE 3

Example	Monomer Composition				
	<i>Ingredient</i>	<i>A-Block</i> (g)	<i>B-Block</i> (g)	<i>Total Batch</i> (g)	<i>phm</i>
4	MAA	446.00	1354	1800.00	60.00
	n-BA	1200.00	0.00	1200.00	40.00
	All MA	0	0	0	0
	Lup - 11			21.00	0.70
	IPA/H <sub>2</sub> O			3000.00	100.00
5	MAA	446.00	1316.5	1762.5	58.75
	n-BA	1200.00	0.00	1200.00	40.00
	All MA	25.0	12.5	37.5	1.25
	Lup - 11			21.00	0.70
	IPA/H <sub>2</sub> O			3000.00	100.00
6	MAA	446.00	1316.5	1762.50	58.75
	n-BA	1200.00	0.00	1200.00	40.00
	EGDMA	25.00	5.0	30.00	1.00
	Lup - 11			30.00	1.00
	IPA/H <sub>2</sub> O			3000.00	100.00

15

Resin of Example 6 was prepared using ethylene glycol dimethacrylate, EGDMA, a difunctional chain extender whose reactive groups have comparable reactivity. The resulting polymer was heavily cross-linked and formed a solid gelled mass during polymerization. The polymer was impossible to isolate and test. In contrast the polymer of Example 5, prepared with allyl methacrylate, formed an easy-to-handle viscous liquid, during polymerization.

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As can be seen from Table 2, varying the composition of monomers allows for the preparation of copolymers of different molecular weights and glass transition temperatures, which permits modification of the desirable properties of the hair styling compositions formulated with the copolymers.

### Examples of Block Copolymers for Hair Styling Aid Formulations

A hair fixative resin should also encompass a number of subjective and objective properties such as curl ease of formulation, sprayability, feel on the hair, washability, curl retention, fast drying and low tack, compatibility with ancillary formulation additives, etc.

The following examples show that blocky/branched copolymers were prepared to demonstrate that, hair fixative polymers with superior performing properties can be obtained by varying the hydrophilic and hydrophobic character of the A and B blocks.

TABLE 4

Example	Monomer Composition				Observations
		A-block	B-block	Total Batch	
	Monomer	(g)	(g)	(g)	phm
7	MAA	531.00	511.50	1042.50	34.75
	AA	144.00	576.00	720.00	24.00
	n-BA	1200.00		1200.00	40.00
	All MA	25.00	12.50	37.50	1.25
	Lup - 11	52.50	0.00	52.50	1.75
	IPA/H <sub>2</sub> O			3000.00	100.00
8	MAA	531.00	511.50	1042.50	34.75
	AA	720.00	0.00	720.00	24.00
	n-BA	1200.00		1200.00	40.00
	All MA	25.00	12.50	37.50	1.25
	Lup - 11	52.50	0.00	52.50	1.75
	IPA/H <sub>2</sub> O			3000.00	100.00
9	MAA	531.00	511.50	1042.50	34.75
	AA	576.00	144.00	720.00	24.00
	n-BA	1200.00		1200.00	40.00
	All MA	25.00	12.50	37.50	1.25
	Lup - 11	52.50	0.00	52.50	1.75
	IPA/H <sub>2</sub> O			3000.00	100.00
10	MAA	209.00	833.50	1042.50	48.75
	AA	720.00	0.00	720.00	10.00



Example	Monomer Composition				Observations
		<i>A-block</i>	<i>B-block</i>	<i>Total Batch</i>	
	<i>Monomer</i>	<i>(g)</i>	<i>(g)</i>	<i>(g)</i>	<i>phm</i>
	n-BA	1200.00		1200.00	50.00
	All MA	25.00	12.50	37.50	1.25
	Lup - 11	52.50	0.00	52.50	1.75
	IPA/H <sub>2</sub> O			3000.00	100.00

Note that by altering the hydrophilic hydrophobic balance of the A-block polymers soluble within a range of pH were made. Polymers that dissolve at relatively lower pH such as the polymers from Examples 8 and 10 are desired for hair fixatives. Polymers that dissolve at higher pH would be more suitable for formulations where high pH is a benefit, i.e., depilatories, medicated creams, etc.

**Sprability:** Hair spray products are typically formulated in hydroalcoholic formulations. It is required that hair fixative resin produces a low viscosity formulations that can be aesthetically delivered in the form a fine spray. The data on Table 5 shows that the Block/Branched copolymers of examples 7, 8, and 9 have better sprayability than current art.

**Hair Feel:** The tactile feel that the hair acquires after been coated with a fixative resin is extremely important. Current polymers tend to leave the hair raspy, dry, gummy, grease, etc. The data in Table 5 shows that the copolymers 7, 8, and 9 have superior feel characteristics. They leave the hair soft and natural.

**Tack:** Most current fixative polymers tend to absorb moisture and therefore become tacky. Note that copolymers 7, 8, and 9 exhibit low tack.

**Flake-off:** Fixative polymers, after drying on hair, exhibit high levels of flakes after combing, giving the hair a dandruff-like appearance. Copolymers 7, 8, and 9 exhibit the lowest levels of flaking.

TABLE 5

(Subjective properties were evaluated directly on hair tressés. 1= worst, 10= best)

Polymer	Hair Feel	Tack	Flake off	Sprayability	% Set Retention 1 hr, 90% RH
PVP, *	3	2	2	1	30.00
Amphomer **	2	3	8	2	80.00
Lovocryl L73 ***	2	3	8	2	50.00
Luv VA73	4	6	6	3	30.00
Luv Hold.	4	6	6	3	30.00
Example 7	6	5	8	6	30.00
Example 8	6	5	8	8	90.00
Example 9	5	5	8	7	84.00
Example 10	5	5	3	3	100.00

\* PVP is polyvinyl pyrrolidone

\*\* Amphomer is a polymer sold by the M.H. Starch Co.

\*\*\* Lovocryl, Luv are trade names for polymers sold by BASF

An important performance property that a hair fixative polymer must also have, is its ability to hold a hairstyle in place at relatively high humidity, i.e., Curl Retention. The curl retention ability of the copolymers of this invention was measured and compared against a number of current hair fixative polymers.

**Curl Retention Protocol:** 0.05 grams of resin dissolved in a hydroalcoholic solution was applied and smeared on clean, 2 grams, 6 in. hair swatches. The swatches were rolled over salon rollers, dried and conditioned overnight. The swatches were mounted inside a humidity chamber at 80°F, and 90 % of relative humidity.

The curl retention was recorded as a function of time and calculated as:

$$L-L(t)/L-L(o) \times 100 = \text{curl retention \%}$$

Where:

L=length of hair fully extended, L(o)=length of hair before exposure to high humidity,  
L(t)=length of hair after exposure at time(t).

As shown in Table 5, the curl retention ability of the blocky-branched copolymers of Examples 8, 9, and 10 was superior to most current fixative polymers.

Copolymer examples 11 and 12, in Table 6, show block copolymers where the A-Block includes 2 ethylhexacrylate (2-EHA) and ethylacrylate (EA), respectively.

TABLE 6

Monomer Composition						Observations
		A-Block	B-Block	Total Batch		
Example	Ingredients	(g)	(g)	(g)	(phm)	
11	MAA	446.00		1316.50	58.75	Soluble in water at pH = 8.02
	2-EHA	1200.00		1200.00	40.00	
	All MA	25.00	12.50	37.50	1.25	
	Lup-11			30.00	1.00	
	IPA/H <sub>2</sub> O			3000.00	100.00	
12	MAA	446.00	1316.50	1762.50	58.75	Soluble in water at pH = 6.61
	EA	1200.00		1200.00	40.00	
	All MA	25.00	12.50	37.50	1.25	
	Lup-11			21.00	1.00	
	IPA/H <sub>2</sub> O			3000.00	100.00	

Low VOC hair styling compositions were prepared using the copolymers of Example 2. The compositions included 3-5 weight percent of a resin containing 60% weight percent of one of the copolymers of Table 2, a solvent system, comprising ethanol and water, and a surfactant, AMP-95. All the compositions were formulated to 50% by weight VOC's. Table 7 lists the components of compositions and summarizes the subjective assessments. The compositions show improved performance over conventional, widely used hair styling formulations. The improved performance is seen in one or more of the following attributes: style retention at high humidity, natural feel, combability, reduced flaking, good styleability and restyleability.

TABLE 7: Hair Styling Compositions Containing 50% VOC

## Composition A

Ingredient	% wt	Comments:
Polymer of Example 1	3.00	Feel of hair is slick initially then it has a very touchable feel when completely dry.
Ethanol	50.00	
Amp 95 *	0.30	
Deionized water	46.70	

\* AMP 95 is amino methyl propanol, 95% wt. in water

**Composition B**

<u>Ingredient</u>	<u>% wt</u>	<u>Comments:</u>
Polymer of Example 2	5.00	Same as for composition A.
Ethanol	50.00	
Amp 95	0.50	
Deionized water	44.50	

**Composition C**

<u>Ingredient</u>	<u>% wt</u>	<u>Comments:</u>
Polymer of Example 3	3.00	Feel of hair is slick initially then becomes touchable when dry. Humidity resistance is greater than for conventional PVP and PVP/vinyl acetate in alcohol formulations.
Ethanol	50.00	
Amp 95	0.17	
Deionized water	46.83	

5

**Composition D**

<u>Ingredient</u>	<u>% wt</u>	<u>Comments:</u>
Polymer of Example 3	5.00	Same as for Composition C.
Ethanol	50.00	
Amp 95	0.29	
Deionized water	44.71	

10

Swatches of hair were sprayed or applied with the hair styling compositions in Table 7. The swatches were evaluated for humidity resistance, expressed in terms of percentage droop (in relation to a fully extended swatch of hair). Subjective assessments of natural feel, combability, resistance to flaking, and restylability/stylability were also made, on a 1 to 10 scale, 10 being the optimum. Table 8 summarizes these characteristics for the four hair styling compositions in Table 7.

**TABLE 8. Hair Styling Properties of Compositions Including the Copolymer**

<u>Composition</u>	<u>Humidity Resistance</u>	<u>Natural Feel</u>	<u>Combability</u>	<u>Flaking</u>	<u>Restylability Stylability</u>
A	30 min - 76% curl drop. 45 min - curl drop	6	9	8	7
B	30 min - 92% curl drop. 1 hr. - curl drop	6	9	7	7
C	7 hrs. - 88% curl drop. 24 hrs. - full droop	6	9	10	8
D	46 hrs - 88% curl drop, 72 hrs. - full droop	6	9	8	8

As seen from Table 8, all of the compositions exhibited better than average natural, feel, combability, resistance to flaking, and stylability/ restylability characteristics. For hair styling compositions employing the same (composition A and B or C and D), these characteristics were rated equally for compositions having lower resin concentration (3%) and those with a higher resin concentration (5%), with the exception of resistance to flaking, which showed a marginal improvement at lower resin concentrations. Humidity resistance was greater at higher resin concentrations.

#### Examples of Reduced VOC Aerosol Hair Fixative Formulations

Example E. 55% VOC Aerosol Hair Spray Using Dimethyl Ether

<u>Item No.</u>	<u>Ingredient</u>	<u>Wt %</u>
1	SD 40-200 Alcohol	25.0
2	Water	35.0
3	Example 5	8.0
4	AMP-95	2.0
5	Dimethyl Ether	30.0

Items 1 thru 4 added and mixed in a container until a clear solution is obtained. This formulation was placed in an aerosol hair spray can. The can was capped with a standard aerosol actuator. Item 5 was pressure charged into the can. Upon discharging the product, the spray pattern was excellent, a very fine aerosol mist was obtained.

Example F. 55% VOC Aerosol Hair Spray Using 152A Propellant

<u>Item No.</u>	<u>Ingredient</u>	<u>Wt %</u>
1	SD 40-200 Alcohol	55.0
2	Polymer of Example 5	8.0
3	AMP-95	2.0
4	Dymel 152A	35.0

Items 1 thru 4 were added and mixed in a container until a clear solution is obtained. This formulation was placed in an aerosol hair spray can. The can was capped with a standard aerosol actuator. Item 5 was pressure charged into the can. Upon discharging the product, the spray pattern was excellent; a very fine aerosol mist was obtained.

## Example G. Styling Mousse

	<u>Item No.</u>	<u>Ingredient</u>	<u>Wt %</u>
	1	Water	81.0
5	2	Polymer of Example 5	3.5
	3	Emulphor on-870	0.5
	4	Propellant A-46	15.0

Item 1 thru 3 were added and mixed in a container until a clear solution is obtained. This  
 10 formulation was placed in an aerosol mousse can. The can was capped with a standard  
 mousse actuator. Item 4 was pressure charged into the can. Upon discharging the  
 product, a thick and creamy foam was obtained.

The following examples are intended to illustrate the range of uses for the  
 15 film forming copolymers of this invention:

Ultrasonic Diagnosis Gel

0.5% Carbomer thickener  
 2.0% Polymer of Example 7  
 0.25% of NaOH  
 20 5.0% of glycerol to 100% with water + preservative

Ointment with Zinc Oxide

1.2% Polymer of Example 10  
 1.0% triethanolamine  
 25 14.0% of zinc oxide to 100% with water + preservative

Furniture Polish

1.0% Polymer of Example 10  
 5.0% silicone oil emulsions (30% strength)  
 30 3.0% carnauba wax emulsion (20% strength) to 100% with water

Domestic Cleaning Agent

1.5% Polymer of Example 10  
 1.3% triethanolamine  
 35 10.0% isopropyl alcohol  
 10.0% nonylphenol + 10 moles of ethylene oxide to 100% water

Water-In-Oil Cream

- 0.5% Polymer of Example 10  
0.1% monoethanolamine  
3.5% diglycerol sesquiisostearate  
5 10.0% paraffin wax  
5.0% ceryl alcohol  
2.2% microwax  
0.2% perfume oil to 100% water + perservative

After Shave Gel

- 10 1.1% Polymer of Example 10  
0.4% monoethanolamine  
35.0% ethyl alcohol  
0.1% menthol to 100% with water + preservative

Hair Shampoo

- 15 0.5% Polymer of Example 10  
0.6% triethanolamine  
12.0% coconut oil alcohol + 10 moles of ethylene oxide  
20 0.1% perfume oil to 100% of water + preservative

Hand Sanitizer

- 1.0% Polymer of Example 10  
65.0% ethyl alcohol  
25 1.5% carbopol  
1.4% triethanolamine  
0.1% perfume oil to 100% with water + preservative

Liquid Oil-In-Water Emulsion

- 30 0.5% Polymer of Example 10  
0.2% NaOH  
5.0% isopropyl palmitate  
5.0% paraffin oil  
5.1% diglycerol stearate + 4 moles of ethylene oxide  
35 0.1% perfume oil to 100% with water + preservative

Oil-In-Water Cream

- 0.7% Polymer of Example 10  
0.6% AMP-95  
40 5.0% petrolatum  
5.2% soybean oil  
3.0% glycerol monostearate  
3.0% tri-stearyl tetraglycol ether ortho-phosphoric acid to 100% with water +  
preservative  
45

Liquid Water-In-Oil Emulsion

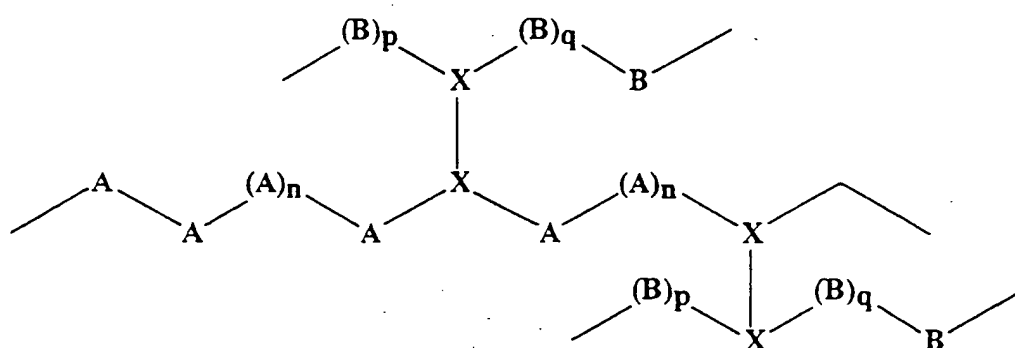
- 0.5% Polymer of Example 10
- 0.6% ammonium hydroxide (10% strength)
- 3.0% hydrogenated castor oil + 7 moles of ethylene oxide
- 5 2.0% polyglyceryl-2 sesquiisostearate
- 1.0% beeswax
- 1.0% mineral oil
- 0.5% magnesium stearate
- 0.5% aluminum montanate
- 10 10.0% isopropyl palmitate
- 15.0% perhydrosqualene to 100% with preservative + water

The invention has been described with reference to the preferred embodiment. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

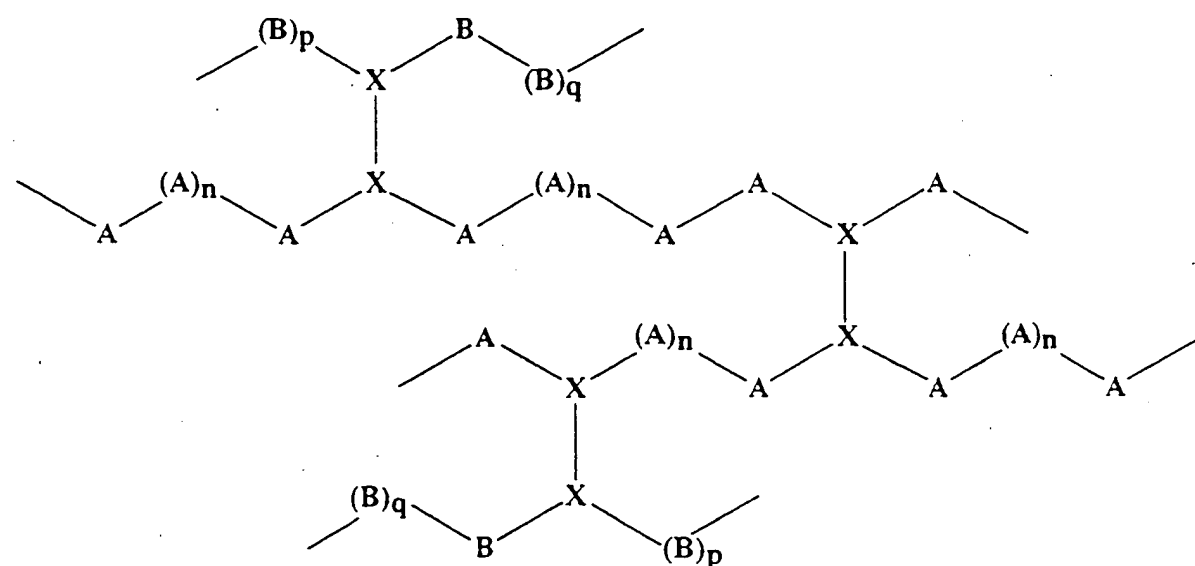


Having thus described the preferred embodiment, the invention is now claimed to be:

1. A film forming block copolymer having a structure selected from the group consisting of the following :



Structure 1:



Structure 2.

wherein A represents the monomer or monomers of a first block, B represents the monomer or monomers of a second block, X represents the extender monomer, n is the degree of polymerization of the A-Block. q and p represent the degree of polymerization

of the B-Block, and either q or p can take the value of zero but not both at the same time, both the A block and the B block are derived from ethylenically unsaturated monomers, the A block is more hydrophobic than the B block, and the copolymer has at least two different glass transition temperatures.

5

2. A film forming block copolymer for application to keratinous substrates which has been prepared by polymerizing:

a polyfunctional monomer or monomers, having at least two functional groups, the reactivity of one functional group being higher than that of other functional group;

10

a first ethylenically unsaturated monomer or monomers which copolymerize preferentially with the functional group of the difunctional monomer which has a higher functionality to form a first block; and

a second ethylenically unsaturated monomer or monomers, which contains at least one carboxylic acid group and copolymerizes with the functional group of the difunctional monomer which has the lesser functionality to form a second block, wherein the first block is more hydrophobic than the second block, and the copolymer has both hydrophobic and hydrophilic blocks, which have at least two different glass transition temperatures.

15

20

3. The copolymer of claim 2, wherein:

the polyfunctional monomer comprises from about 0.005 to 2 mole percent of the total monomers;

the first ethylenically unsaturated monomer comprises from about 5 to about 95 mole percent of the total monomers; and,

25

the second ethylenically unsaturated monomer comprises from about 5 to about 70 mole percent of the total monomers.

4. The copolymer of claim 2, wherein:

the polyfunctional monomer comprises from 0.1 to 1.5 mole percent of the total monomers;

30

the first ethylenically unsaturated monomer comprises from 5 to 50 mole percent of the total monomers; and,

the second ethylenically unsaturated monomer comprises from 10 to 70 mole percent of the monomers.

5

5. The copolymer of claim 2, wherein the copolymer has a molecular weight of less than 1,000,000.

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6. The copolymer of claim 2, wherein the first block has a molecular weight of 10,000 to 100,000.

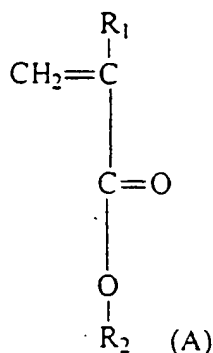
7. The copolymer of claim 2, wherein the second block has a molecular weight of 1,000 to 100,000.

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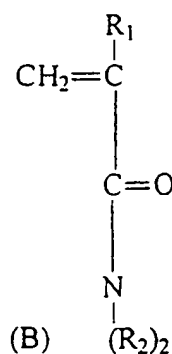
8. The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of monomers having at least 2 to 30 carbon atoms.

20

9. The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of:  
acrylate and methacrylate esters and acids;  
N-substituted acrylamides, substituted with alkyl radicals containing from 2 to 12 carbon atoms; and,  
esters having the general formula:



or



25

where  $R_1$  is selected from the group consisting of -H, -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>, and,

$R_2$  is an aliphatic hydrocarbon functional group having at least two carbons, such as C<sub>1</sub> to C<sub>20</sub> alkyls and cycloalkyls; polynuclear aromatic hydrocarbon groups such as naphthyls; alkylaryls wherein the alkyl has one or more carbons, preferably 4 to 8 carbons; haloalkyls of 4 or more carbons, such as perfluoroalkyls; polyalkyleneoxy groups wherein alkylene is propylene or higher alkylene and there is at least 1 alkyleneoxy unit per hydrophobic moiety; and combinations thereof.

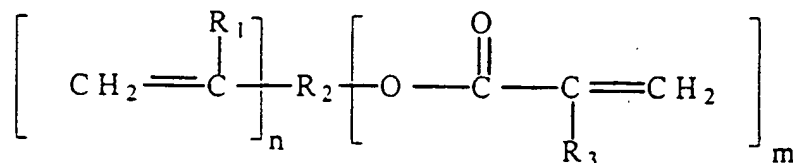
10                    10.    The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of the higher alkyl esters of  $\alpha,\beta$ -ethylenically unsaturated carboxylic acids; ethyl half ester of maleic anhydride; diethyl maleate; alkyl esters derived from the reactions of alkanols having from 2 to 20 carbon atoms with ethylenically unsaturated carboxylic acids; alkylaryl esters of  
15    ethylenically unsaturated carboxylic acids; N-alkyl, ethylenically unsaturated amides;  $\alpha$ -olefins; vinyl alkylates wherein the alkyl has at least 8 carbons; vinyl alkyl ethers; N-vinyl amides; and ar-alkylstyrenes; and combinations thereof.

20                    11.    The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is an acrylamide or methacrylamide selected from the group consisting of N-ethyl acrylamide, N-tertiary-octyl acrylamide, N-decyl acrylamide, N-dodecyl acrylamide, N-ethyl methacrylamide, N-tertiary octyl methacrylamide, N-decyl methacrylamide, N-dodecyl methacrylamide, and combinations thereof.

25                    12.    The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of alkyl esters of acrylic acid, methacrylic acid, mono or di-alkyl acrylamides, and mono or di-alkyl methacrylamides, wherein the alkyl has from 2 to 8 carbon atoms; alkyl styrenes, wherein alkyl has from 4 to 8 carbons, such as t-butyl; and combinations thereof.

30                    13.    The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of n-butyl acrylate, t-butyl acrylate, ethyl acrylate, 2-hexyl acrylate, and combinations thereof.

14. The copolymer of claim 2, wherein the polyfunctional monomer has the general formula:



5

where n and m are integers from 1 to 4;

R<sub>1</sub>, R<sub>3</sub> are selected from the group consisting of H and alkyl; and,

R<sub>2</sub> is selected from the group consisting of alkyl, cycloalkyl, aryl,  
 -(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>p</sub>- where p = 1 to 50, -(CH<sub>2</sub>(CH<sub>3</sub>)-CH<sub>2</sub>-O)<sub>p</sub>- where p = 1 to 50,  
 amido, ester, polyamido, and polyester.

10

15. The copolymer of claim 2, wherein the polyfunctional monomer is selected from the group consisting of allyl methacrylate, allyl acrylate, vinyl methacrylate, vinyl acrylate, vinyl acrylamide, vinyl methacrylamide, allyl methacrylamide, allyl acrylamide, and mixtures thereof.

15

16. The copolymer of claim 2, wherein the reactivity of the first functional group is from about three to ten times more than the reactivity of the second functional group, allyl or vinyl.

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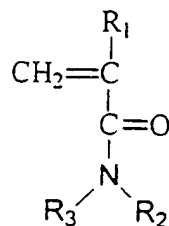
17. The copolymer of claim 2, wherein the first functional group is an allyl vinyl group and wherein the second functional group is selected from the group consisting of methacrylic and acrylic functional groups.

25

18. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is sufficiently water soluble or dispersible to form at least a 20 weight percent solution when dissolved in water.

19. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of:

1) ethylenically unsaturated amides of the general formula:



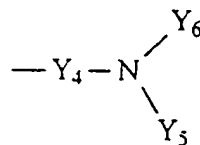
where  $R_1$  is selected from the group consisting of -H, -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, branched or linear alkyl, aryl, and cycloalkyl;

$R_2$  and  $R_3$  are selected from the group consisting of:

-H, -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, branched alkyl, linear alkyl, aryl, cycloalkyl;

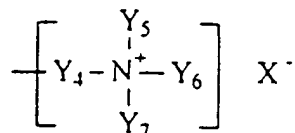
acid or salt functional groups, such as -SO<sub>3</sub>H, -SO<sub>3</sub> M (where M = metal);

amino functional groups of the general formula:



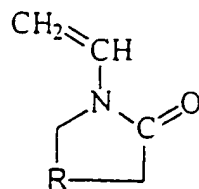
where  $Y_4$ ,  $Y_5$ ,  $Y_6$  are -H, -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, branched or linear alkyl, aryl, cycloalkyl, and combinations thereof;

and quaternized amino functional groups of the general formula:



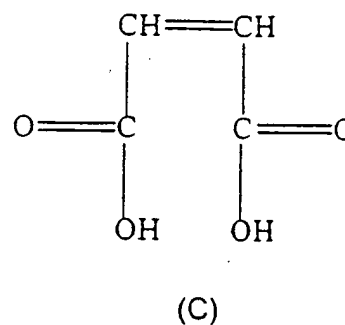
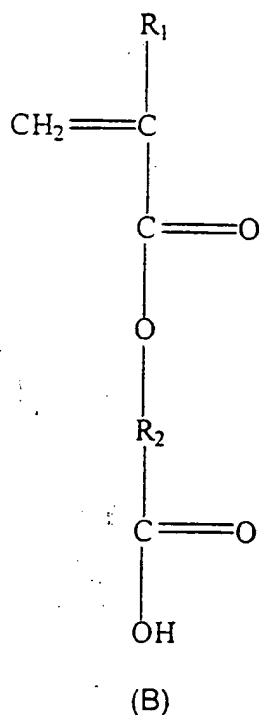
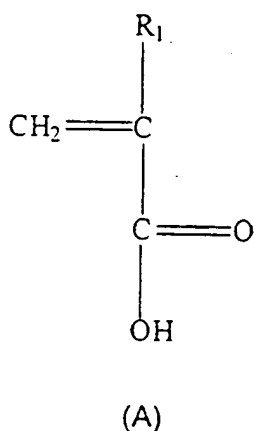
where  $Y_4$ ,  $Y_5$ ,  $Y_6$  are -H, -CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>3</sub>, branched or linear alkyl, aryl, cycloalkyl, and combinations thereof;

2) ethylenically unsaturated water soluble heterocyclic of the general formula:



where R is an alkylene group, such as  $R_2 = -[CH_2-]_n$ , where n is an integer from 1 to 4; and,

3) ethylenically unsaturated carboxylic acids of one of the three general formulae:



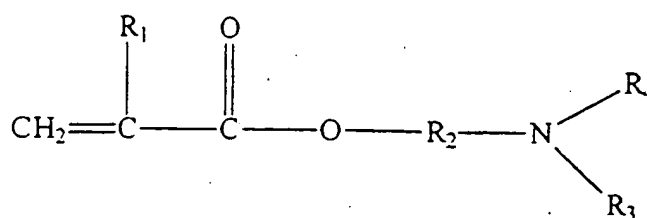
where  $R_1$  is selected from the group consisting of -H, -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>3</sub>;

$R_2$  is selected from the group consisting of -[CH<sub>2</sub>]-<sub>n</sub>, where n is an integer from 1 to 40; linear or branched alkyl; cycloalkyl; aryl; polyethylene oxide, such as -(CH<sub>2</sub>-CH<sub>2</sub>-O)<sub>p</sub>- where p = 1 to 50; and polypropylene oxide, such as -(CH<sub>2</sub>(CH<sub>3</sub>)-CH<sub>2</sub>-O)<sub>p</sub>- where p = 1 to 50.

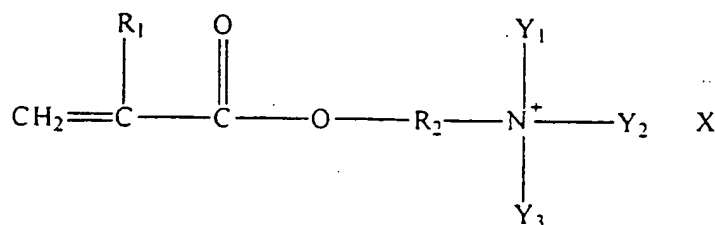
20. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is an ethylenically unsaturated amide selected from the group consisting of acrylamide, methacrylamide and fumaramide, and their N-substituted derivatives, such as 2-acrylamido-2-methylpropane sulfonic acid, N-(dimethylaminomethyl) acrylamide; N-(trimethylammonium-methyl) acrylamide chloride; and N-(trimethylammoniumpropyl)-methacrylamide chloride.

21. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is a heterocyclic amide selected from the group consisting of vinyl pyrrolidone and vinyl caprolactam.

22. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is an ethylenically unsaturated carboxylic acid selected from the group consisting of: acrylic acid; methacrylic acid; maleic acid; itaconic acid; vinylaryl sulfonic acid, salts of ethylenically unsaturated quaternary ammonium compounds, such as vinylbenzyl trimethyl ammonium chloride; sulfoalkyl esters of unsaturated carboxylic acids, and aminoalkyl esters of unsaturated carboxylic acids of the general formula:



and quaternized salts of unsaturated carboxylic acids of the general formula:



where  $\text{R}_1$  is selected from the group consisting of -H, - $\text{CH}_3$ , - $\text{CH}_2\text{CH}_3$ ;

$\text{R}_2$  is selected from the group consisting of  $-\text{[CH}_2\text{]}_n$ , where  $n$  is an integer from 1 to 40; linear alkyl; branched alkyl; cycloalkyl; aryl; polyethylene oxide, such as  $-(\text{CH}_2-\text{CH}_2-\text{O})_p$  where  $p$  is an integer from 1 to 50, polypropylene oxide such as  $-(\text{CH}_2(\text{CH}_3)-\text{CH}_2-\text{O})_p$  where  $p$  is an integer from 1 to 50; and combinations thereof;

$\text{Y}_4$ ,  $\text{Y}_5$ , and  $\text{Y}_6$  are selected from the group consisting of -H, - $\text{CH}_3$ , - $\text{CH}_2\text{CH}_3$ , branched or linear alkyl, aryl, cycloalkyl, and combinations thereof; and



X is an acid radical selected from the group consisting of chloride, bromide, sulfate, sulfonate, phosphate, methyl, and ethyl sulfonate.

23. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of 2-aminoethyl methacrylate; N,N-dimethyl-aminoethyl methacrylate; N,N-dimethyl aminoethyl acrylate; 2-tert-butyl aminoethyl methacrylate; 2-trimethylammonium ethylmethacrylate chloride; 2-trimethylammonium ethylacrylate chloride; vinyl amines, such as vinyl pyridine and vinyl morpholine; diallyl amines; and diallyl ammonium compounds, such as diallyl dimethyl ammonium chloride.

24. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, C<sub>1</sub>-C<sub>4</sub> alkyl half esters of maleic and fumaric acids, and combinations thereof.

25. The copolymer of claim 2, wherein the polyfunctional monomer is allyl methacrylate, the first ethylenically unsaturated monomer is a mixture of n-butyl acrylate and (meth)acrylic acid and the second ethylenically unsaturated monomer is selected from the group consisting of acrylic acid, methacrylic acid and mixtures thereof.

26. A block copolymer adaptable for use in forming a hair styling composition, the copolymer having a plurality of glass transition temperatures, the copolymer including:

a hydrophobic organic polymeric block; and

hydrophilic organic block.

27. A hair styling composition including:

from about 0.01-20% by weight of a copolymer which has been prepared

utilizing:

a polyfunctional monomer having at least a first functional group and a second functional group, the reactivity of the first functional group being higher than that of the second functional group;

5 a first ethylenically unsaturated monomer which copolymerizes preferentially with the first functional group of the difunctional monomer to form a first, hydrophobic block; and

a second ethylenically unsaturated monomer which is hydrophilic and copolymerizes with the second functional group of the difunctional monomer to form a second block and a copolymer having both hydrophobic and hydrophilic blocks.

10

28. The hair styling composition of claim 27, wherein the polyfunctional monomer comprises from about 0.005 to 2 mole percent of the total monomers;

15 the first ethylenically unsaturated monomer comprises from about 30 to about 95 mole percent of the total monomers; and,

the second ethylenically unsaturated monomer comprises from about 5 to about 80 mole percent of the total monomers.

20 29. The hair styling composition of claim 27, further including at least one of the following materials:

0 to 25 weight percent of an emulsifier;

0.05 to 99% solvents;

0.05 to 10% rheology modifiers;

0.05 to 5% neutralizing agents;

25 0-60 weight percent of a liquid propellant or gas; and,

0-1% of a surfactant.

30 30. A hair styling composition including:

from about 0.5 to 99 weight percent water or water and alcohol; and

from about .01 to 20 weight percent of a block copolymer, the copolymer having a plurality of glass transition temperatures. the copolymer including:

a hydrophobic organic block; and  
hydrophilic organic block joined to the hydrophobic block..

5 31. The hair styling composition of claim 30, wherein the hydrophobic block is a polyacrylate.

32. A method of preparing a hair styling composition, the method including preparing a copolymer having hydrophobic and hydrophilic blocks by copolymerizing:

10 a polyfunctional monomer having at least a first functional group and a second functional group, the reactivity of the first functional group being higher than that of the second functional group;

15 a first ethylenically unsaturated monomer which is an ethylenically unsaturated monomer which copolymerizes preferentially with the functional group of the difunctional monomer having the higher reactivity to form a first hydrophobic block; and

a second ethylenically unsaturated monomer which has at least one carboxylic acid group and copolymerizes with the second functional group to form a copolymer having both hydrophobic and hydrophilic blocks.

20

33. The method of claim 32, wherein the preparing the copolymer includes:

25 adding to a reaction vessel, a solvent, the polyfunctional monomer or monomers, the first ethylenically unsaturated monomer or monomers, and an initiator; reacting the monomers to form a first block;

adding a second ethylenically unsaturated monomer or monomers having at least one carboxylic acid group; and,

30 reacting the monomers to form a second block and a copolymer having both hydrophobic and hydrophilic groups and at least two glass transition temperatures.

34. The method of claim 33, wherein the initiator is selected from the group consisting of azo-type initiators and peroxy-type initiators.

35. The method of claim 34, wherein the initiator is an azo-type initiator selected from the group consisting of azobis-dimethylvaleronitrile, azobis-isobutyronitrile, azobis-methylbutyronitrile, and combinations thereof.

5

36. The method of claim 34, wherein the initiator is a peroxo-type initiator selected from the group consisting of di-T butyl peroxide, T-butyl cumyl peroxide, T-butyl peroxy-pivalate, lauryl peroxide, cumene hydroperoxide, ethyl hexyl peroxodicarbonate, diisopropyl peroxydicarbonate, 4-(t-butylperoxylperoxy-carbonyl)-3-hexyl-6-7-(t-butylperoxycarbonyl)heptyl cyclohexene, cumene hydroperoxide and t-butyl peroxyneodecanoate, t-butyl hydroperoxide, benzoyl peroxide, and combinations thereof.

10

37. The method of claim 36, wherein the initiator is t-butyl peroxy-pivalate.

15

38. The method of claim 34, wherein the initiator is at a concentration of from about 0.005 to 1 mole percent of the total monomers.

20

39. The method of claim 33, wherein the solvent is selected from the group consisting of water, hydrocarbons, alcohols, ethers, esters, aromatic solvents, glycols, glycol ethers, glycol esters, and combinations thereof.

25

40. The method of claim 39, wherein the solvent also includes water.

41. The method of claim 39, wherein the solvent is selected from the group consisting of water, ethyl alcohol, isopropyl alcohol, t-butyl alcohol, ethyl acetate, methyl acetate, butyl acetate, benzene, toluene, methylene chloride, hexane, cyclohexane, mineral spirits, and combinations thereof.

30

42. The method of claim 39, wherein the solvent is isopropyl alcohol and water.

43. The method of claim 33, wherein the copolymer is produced in the same reaction vessel.

5 44. The method of claim 33, further including neutralizing the copolymer so that between 0.1 and 100 percent of the carboxylic acid groups are neutralized.

10 45. A method of preparing a hair styling composition, the method including:

preparing a block copolymer, the copolymer having a plurality of glass transition temperatures, the copolymer including:

a hydrophobic organic polymeric block; and

hydrophilic organic block;

15 combining about 1-10 percent of the copolymer with from about 20 to 97 weight percent of water and from about 0 to 80 weight percent of an organic solvent.

20 46. The copolymer of claim 2, wherein the first ethylenically unsaturated monomer is selected from the group consisting of methyl acrylate, methyl methacrylate, butyl acrylate, ethyl acrylate, octyl acrylate, dodecyl acrylate, dodecyl methacrylate, tridecyl acrylate, tridecyl methacrylate, tetradecyl acrylate, tetradecyl methacrylate, octadecyl acrylate, octadecyl methacrylate, alkyl esters derived from the reactions of alkanols having from 2 to 20 carbon atoms with acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, itaconic acid and aconitic acid, nonyl  $\alpha$ -phenyl  
25 acrylate, nonyl- $\alpha$ -phenyl methacrylate, dodecyl- $\alpha$ -phenyl acrylate and dodecyl- $\alpha$ -phenyl methacrylate, N-butyl acrylamide, T-butyl acrylamide, octyl acrylamide, N-octadecyl acrylamide, N-octadecyl methacrylamide, N,N-dioctyl acrylamide, octene-1, decene-1, dodecene-1, hexadecene-1, vinyl laurate, vinyl stearate, dodecyl vinyl ether, hexadecyl vinyl ether, N-vinyl lauramide, N-vinyl stearamide, t-butyl styrene, and combinations  
30 thereof.

47. The copolymer of claim 2, wherein said first block has a glass transition temperature which is less than the glass transition temperature of said second block.

48. The copolymer of claim 2, wherein the polyfunctional monomer has a fast reacting unsaturated group of the acrylate or methacrylate type and a slower reacting group of the allyl type.

49. The copolymer of claim 2, wherein said polyfunctional monomer is allyl methacrylate.

50. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a blend of hydrophobic and hydrophilic monomers.

51. The copolymer of claim 2, wherein the second ethylenically unsaturated monomers are a blend of hydrophilic, ionizable monomers.

52. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a mixture of n-butyl acrylate and methacrylic acid.

53. The copolymer of claim 52, wherein said acid monomer comprises 50 mole % or less of said monomer mixture.

54. The copolymer of claim 2, wherein the second ethylenically unsaturated monomers are a blend of acrylic acid and methacrylic acid.

55. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a mixture of n-butyl acrylate and methacrylic acid, the second ethylenically unsaturated monomers are a blend of acrylic acid and methacrylic acid, and the acid monomers comprise about 50 to about 70 mole % of the total monomers.

56. The copolymer of claim 2, wherein said first block has a glass transition temperature of about 30 °C or less and said second block has a glass transition temperature of greater than 30 °C.

57. The copolymer of claim 2, wherein said first block has a glass transition temperature of about 0 °C or less and said second block has a glass transition temperature of greater than 0 °C.

5

58. The copolymer of claim 50, wherein said hydrophilic monomer comprises 60% by weight or less of the blend of hydrophobic and hydrophilic monomers.

10

59. The copolymer of claim 2, wherein the first ethylenically unsaturated monomers are a mixture of n-butyl acrylate and methacrylic acid, the second ethylenically unsaturated monomers are a blend of acrylic acid and methacrylic acid, and the acid monomers comprise about 50 to about 50 mole % of the total monomers.

15

60. The copolymer of claim 2, wherein the second ethylenically unsaturated monomer is selected from the group consisting of vinylbenzyl sulfonic acid, vinylbenzyl trimethyl ammonium chloride, and 2-sulfoethyl methacrylate.

# INTERNATIONAL SEARCH REPORT

In International Application No  
PCT/US 99/30790

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F265/04 C08F291/00 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 484 053 A (GOLDSCHMIDT AG TH) 24 August 1977 (1977-08-24)  examples ---	1-3, 8-10, 12-18, 22,24, 25,46-55
X	US 5 225 456 A (LANGERBEINS KLAUS ET AL) 6 July 1993 (1993-07-06) claims 1,7; example 4 ---	1-4
X	US 5 403 894 A (TSAI MIN-CHI ET AL) 4 April 1995 (1995-04-04) column 4, line 3 -column 5, line 62; examples --- -/-	1-19

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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\*P\* document published prior to the international filing date but later than the priority date claimed

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/30790

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 398 576 A (ROHM & HAAS) 22 November 1990 (1990-11-22) page 7, line 1-23 page 7, line 52 -page 8, line 3; examples	1-60
X	US 4 130 517 A (LUNDBERG ROBERT D ET AL) 19 December 1978 (1978-12-19) column 1, line 13-31 column 9, line 59-68	26
X	US 4 085 167 A (LEWIS SHELDON N ET AL) 18 April 1978 (1978-04-18) column 3, line 19-25 column 1, line 26-55 column 2, line 38-51	1,2
X	EP 0 233 014 A (ALLIED COLLOIDS LTD) 19 August 1987 (1987-08-19) column 7, line 26-62 column 8, line 11-19 column 8, line 50-61	1-4,8-18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In ternational Application No  
PCT/US 99/30790

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1484053 A	24-08-1977	DE 2352243 A	24-04-1975
		AT 334100 B	27-12-1976
		AT 812074 A	15-04-1976
		BE 820813 A	03-02-1975
		BR 7408662 A	04-11-1975
		CH 615967 A	29-02-1980
		FR 2248155 A	16-05-1975
		IT 1021688 B	20-02-1978
		NL 7413730 A	22-04-1975
		SE 400588 B	03-04-1978
		SE 7413031 A	21-04-1975
US 5225456 A	06-07-1993	DE 3902557 A	02-08-1990
		AT 105846 T	15-06-1994
		DE 59005698 D	23-06-1994
		DK 381030 T	20-06-1994
		EP 0381030 A	08-08-1990
		ES 2055174 T	16-08-1994
		JP 2240174 A	25-09-1990
		JP 2801339 B	21-09-1998
US 5403894 A	04-04-1995	AT 135019 T	15-03-1996
		AU 657965 B	30-03-1995
		AU 1869392 A	14-01-1993
		BR 9202580 A	16-03-1993
		CA 2073154 A	12-01-1993
		CN 1068337 A, B	27-01-1993
		CZ 9202170 A	13-01-1993
		DE 69208754 D	11-04-1996
		DE 69208754 T	19-09-1996
		EP 0522791 A	13-01-1993
		ES 2086657 T	01-07-1996
		FI 923192 A	12-01-1993
		HK 160996 A	06-09-1996
		HU 214105 B	29-12-1997
		IL 102469 A	30-03-1995
		JP 5194681 A	03-08-1993
		KR 149877 B	15-05-1999
		MX 9204036 A	01-01-1993
		NO 922664 A	12-01-1993
		NZ 243439 A	26-10-1994
		PL 171898 B	30-06-1997
		SK 217092 A	08-02-1995
		ZA 9204957 A	31-03-1993
EP 0398576 A	22-11-1990	AT 125826 T	15-08-1995
		AU 631635 B	03-12-1992
		AU 5497590 A	15-11-1990
		BR 9002257 A	30-07-1991
		CA 2015832 A	15-11-1990
		CN 1047322 A	28-11-1990
		DE 69021266 D	07-09-1995
		DE 69021266 T	04-01-1996
		HK 172495 A	17-11-1995
		JP 2845570 B	13-01-1999
		JP 3072511 A	27-03-1991
		MX 171904 B	22-11-1993
		NO 902063 A	16-11-1990

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/30790

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0398576 A		NZ 233653 A	27-01-1993
		PT 94033 A	08-01-1991
		TR 24993 A	01-09-1992
		US 5266646 A	30-11-1993
		ZA 9003607 A	30-01-1991
US 4130517 A	19-12-1978	BE 810222 A	29-07-1974
		CA 1043039 A	21-11-1978
		DE 2403934 A	08-08-1974
		FR 2215442 A	23-08-1974
		GB 1458584 A	15-12-1976
		IT 1007121 B	30-10-1976
		JP 49107044 A	11-10-1974
		NL 7401195 A	31-07-1974
		US 4057598 A	08-11-1977
		US 4104824 A	08-08-1978
US 4085167 A	18-04-1978	AR 200665 A	29-11-1974
		AU 476006 B	09-09-1976
		AU 6271073 A	22-05-1975
		BE 808255 A	05-06-1974
		CA 1006299 A	01-03-1977
		DE 2357615 A	12-06-1974
		ES 421135 A	16-10-1976
		FR 2209788 A	05-07-1974
		GB 1447556 A	25-08-1976
		IL 43760 A	31-07-1977
		IT 1003271 B	10-06-1976
		JP 49099188 A	19-09-1974
		KR 7900286 A	16-04-1979
		NL 7316672 A	10-06-1974
		SE 403619 B	28-08-1978
		TR 17712 A	23-07-1975
		US 4167502 A	11-09-1979
		ZA 7308651 A	30-04-1975
EP 0233014 A	19-08-1987	JP 62230813 A	09-10-1987